

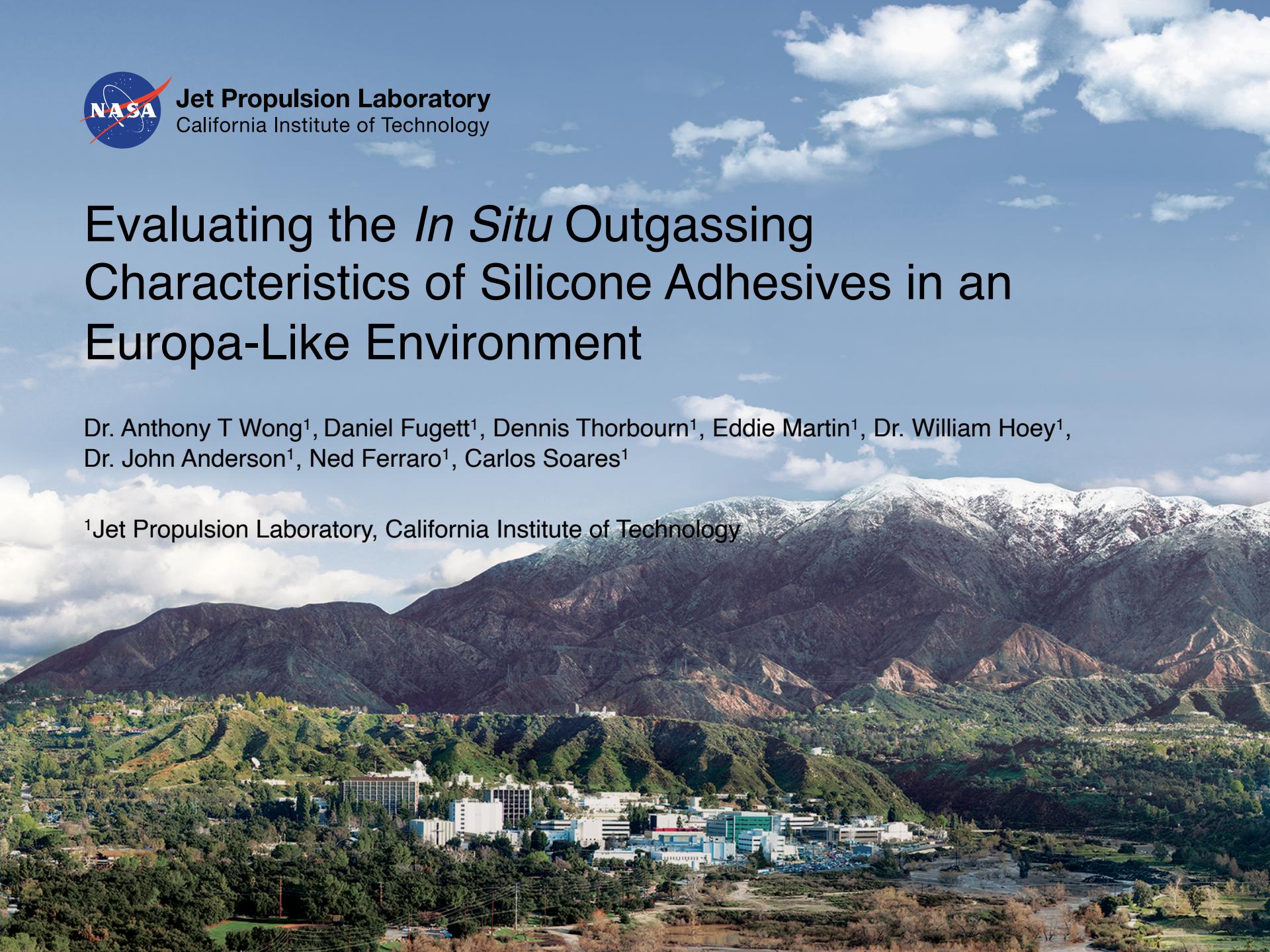


Jet Propulsion Laboratory
California Institute of Technology

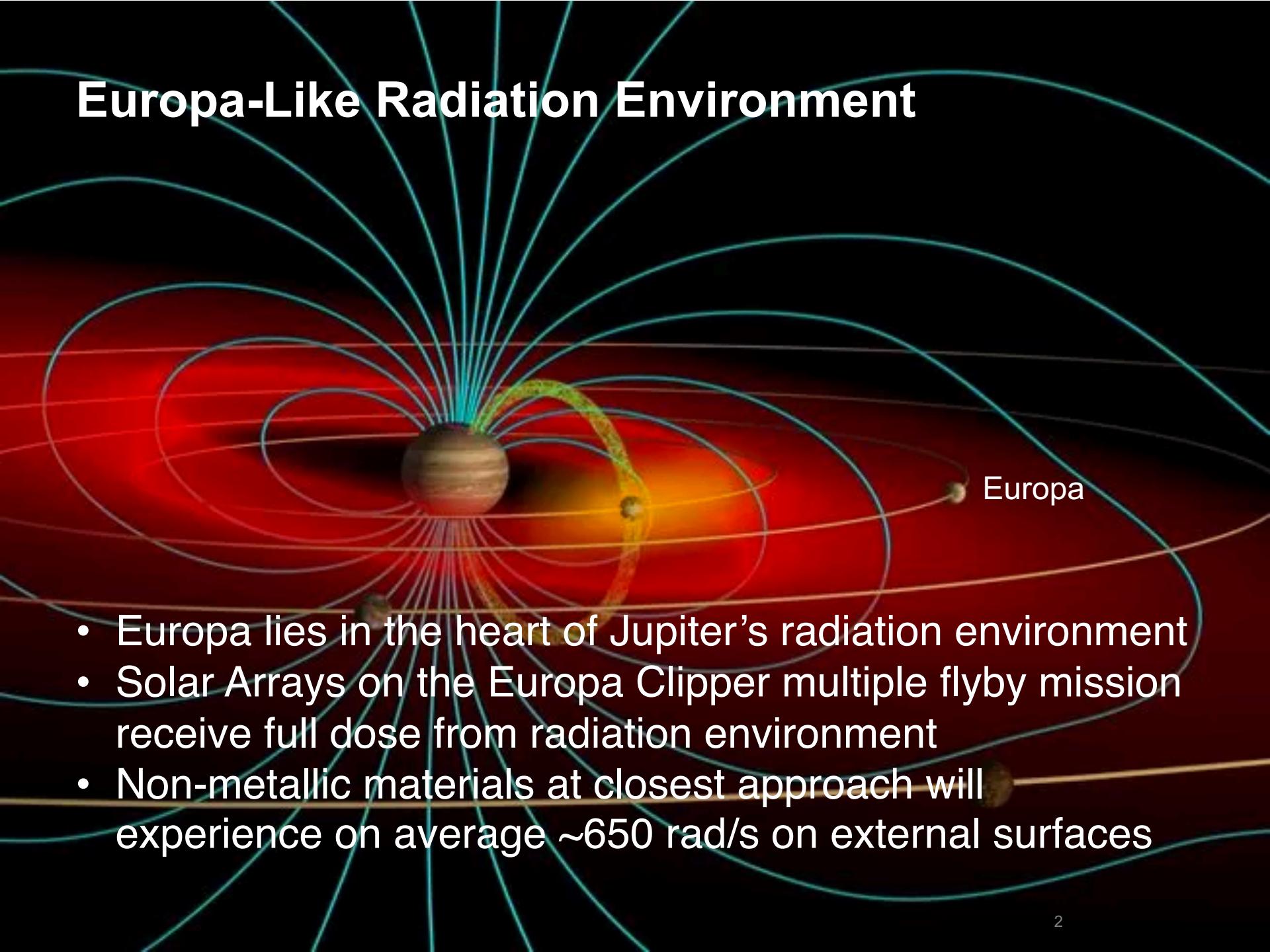
Evaluating the *In Situ* Outgassing Characteristics of Silicone Adhesives in an Europa-Like Environment

Dr. Anthony T Wong¹, Daniel Fugett¹, Dennis Thorbourn¹, Eddie Martin¹, Dr. William Hoey¹, Dr. John Anderson¹, Ned Ferraro¹, Carlos Soares¹

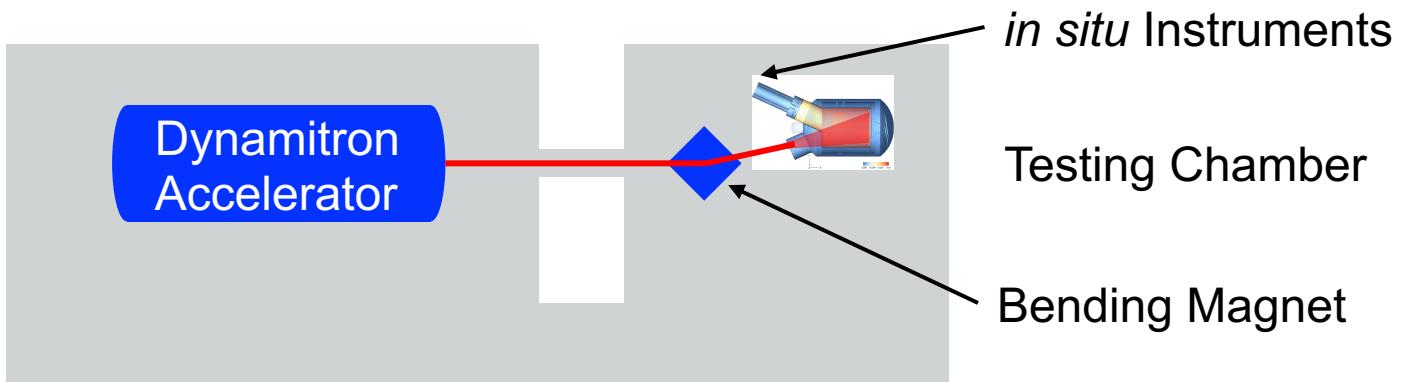
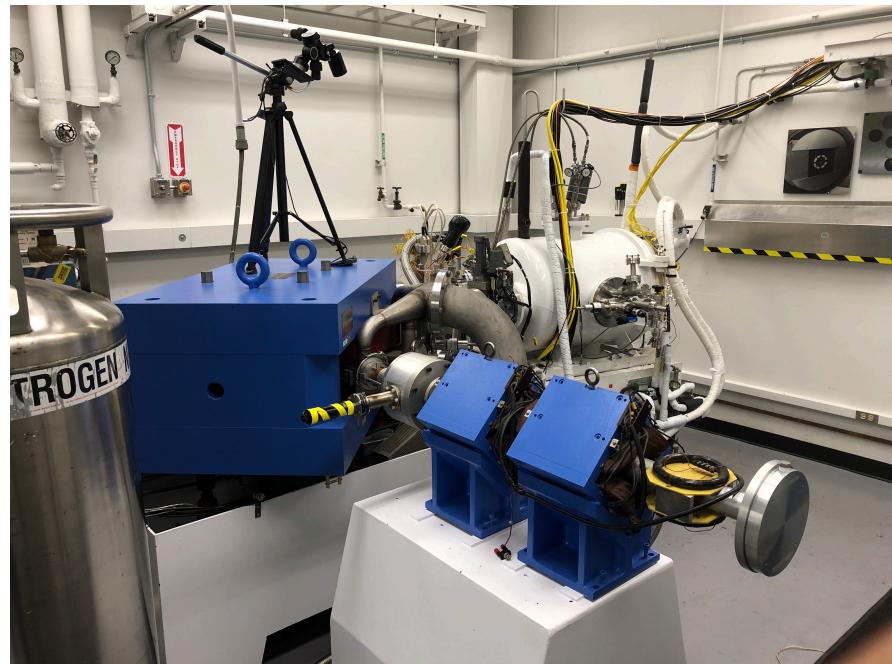
¹Jet Propulsion Laboratory, California Institute of Technology



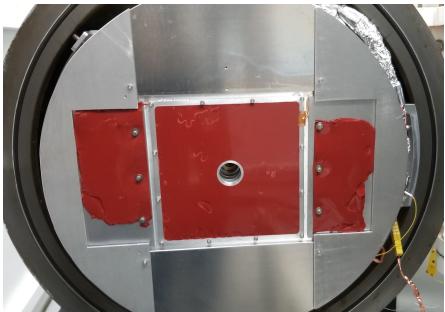
Europa-Like Radiation Environment

- 
- The diagram illustrates the complex magnetic environment around Jupiter. A large, brownish-yellow sphere represents Jupiter at its center. Numerous blue lines radiate from the planet, representing the lines of force of its magnetic field. These lines are highly distorted and compressed on the side facing Europa, creating a bright red glow. Europa, a small grey sphere, is shown in orbit around Jupiter, positioned on the right side of the diagram. The background is black, with the increasing intensity of the red glow from Jupiter's magnetosphere extending towards the bottom right.
- Europa lies in the heart of Jupiter's radiation environment
 - Solar Arrays on the Europa Clipper multiple flyby mission receive full dose from radiation environment
 - Non-metallic materials at closest approach will experience on average ~650 rad/s on external surfaces

Radiation Induced Outgassing Test (RIOT) Setup

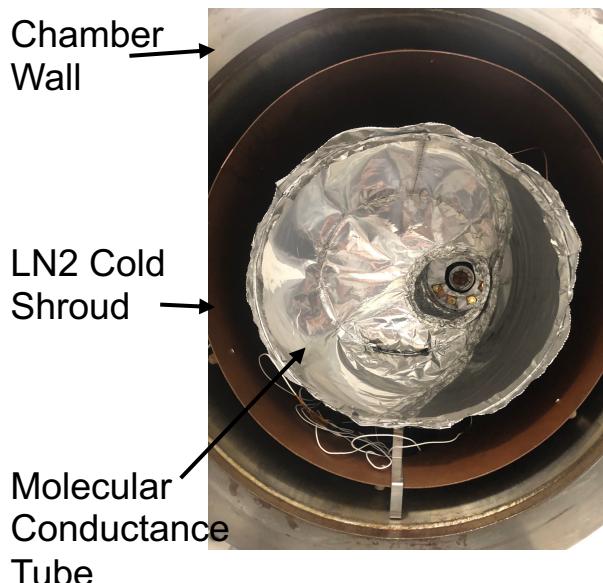
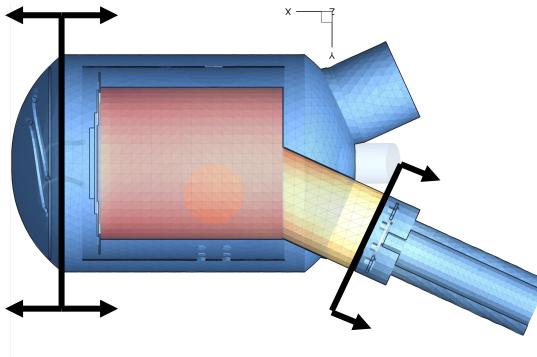


Test Chamber Configuration



Sample Under Test

- LN2 Cold Shroud used to getter residual vapors in chamber
- Molecular Conductance Tube held at elevated temperature using strip heaters to keep sample outgassing constituents from sticking to cold shroud
- Molecular transport ray tracing model used to calculate the transmission fraction from sample to instruments
(ASEC Presentation on Friday at 8:50 am by Dr. William Hoey)



Extrel MAX 1000
Quadrupole Mass
Spectrometer

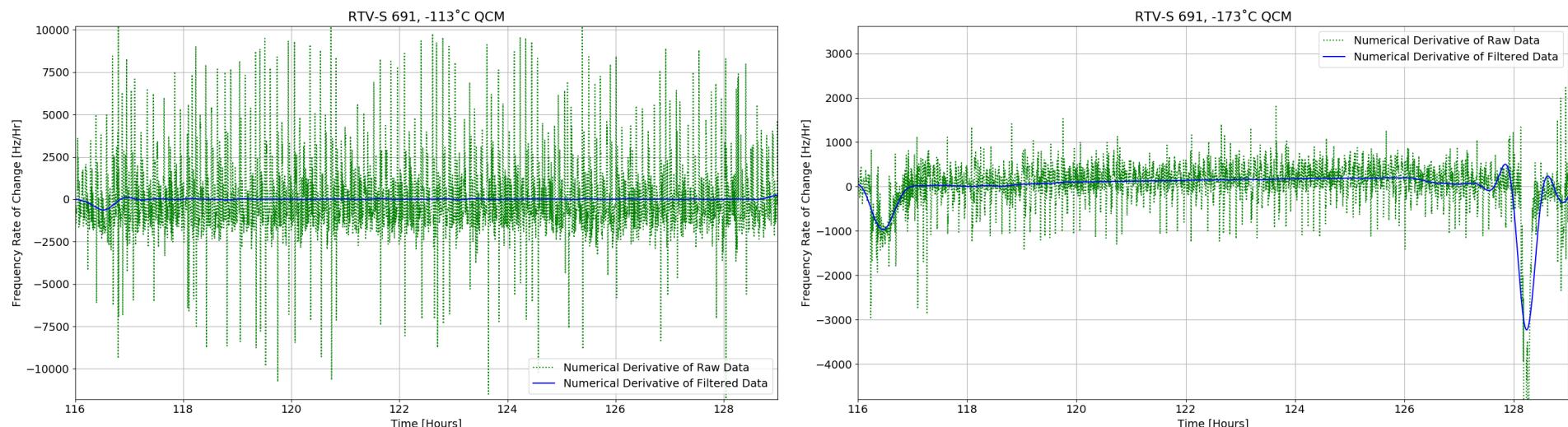


-133°C -93°C -113°C -173°C
QCM Research MK 18 Cryo
Quartz Crystal Microbalances
(CQCM)

Testing Parameters and Procedures

- Sample Temperature: $-113 \pm 5^\circ\text{C}$
 - Mimics material temperature during Europa flyby
- Electron Energy: 1.5MeV
 - High enough energy to dose samples without imparting charge
- Electron Flux: $2.6\text{E}10 \text{ e-}/\text{cm}^2/\text{s}$
 - Mimics peak flux for average Europa flyby
- Duration: Nominal 8 hour irradiation
 - Maximum time duration for nominal facility operation
 - Average flyby will experience >20 hour irradiation at peak flux

RIOT Instrumentation: CQCMs



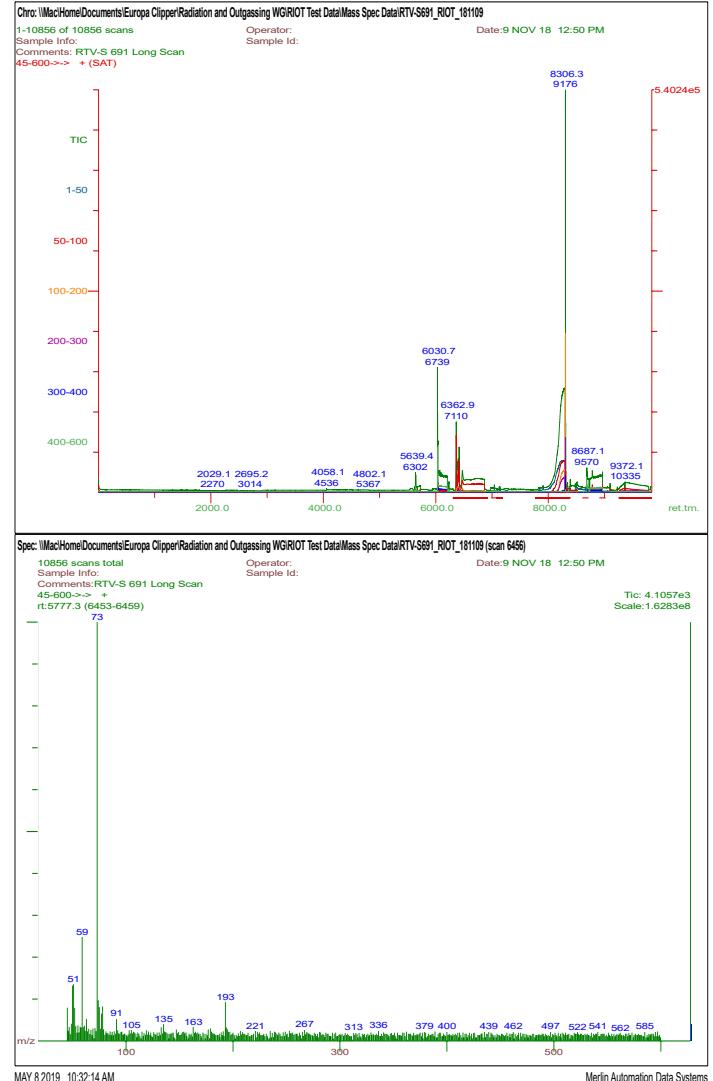
QCM at Temperature

Electron Beam On

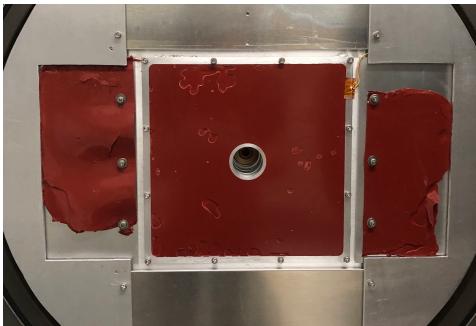
- Data are logged through duration of a test run, sometimes as high as 168 hours
- Segments of time are identified as measurement periods
- Raw Frequency Data is often noisy due to limitations in the instrumentation setup
- Low Pass filters are used to reduce signal noise during analysis

RIOT Instrumentation: Mass Spectrometer

- Extrel MAX 1000 Quadrupole Mass Spectrometer
- Nominal Scan Range m/z of 1-600
- Phase 1 tests collected centroid data
- Phase 2 tests collected spectra data
- Spectrometer pre-amplifier and multiplier settings adjusted during testing to maximize signal to noise for any given test parameter
- Similar to QCMs, data logged continuously through entire test run



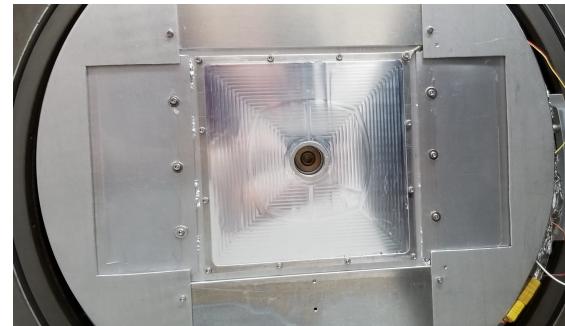
Tested Samples



Wacker RTV-S 691



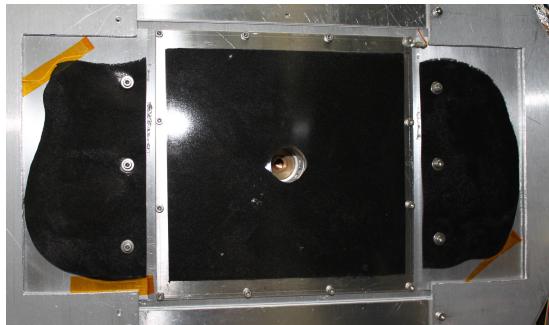
Nusil SCV-2585



Dow Corning 93-500



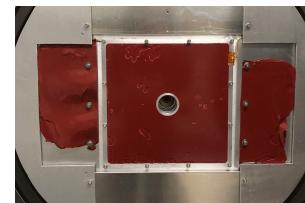
Nusil CV-1500



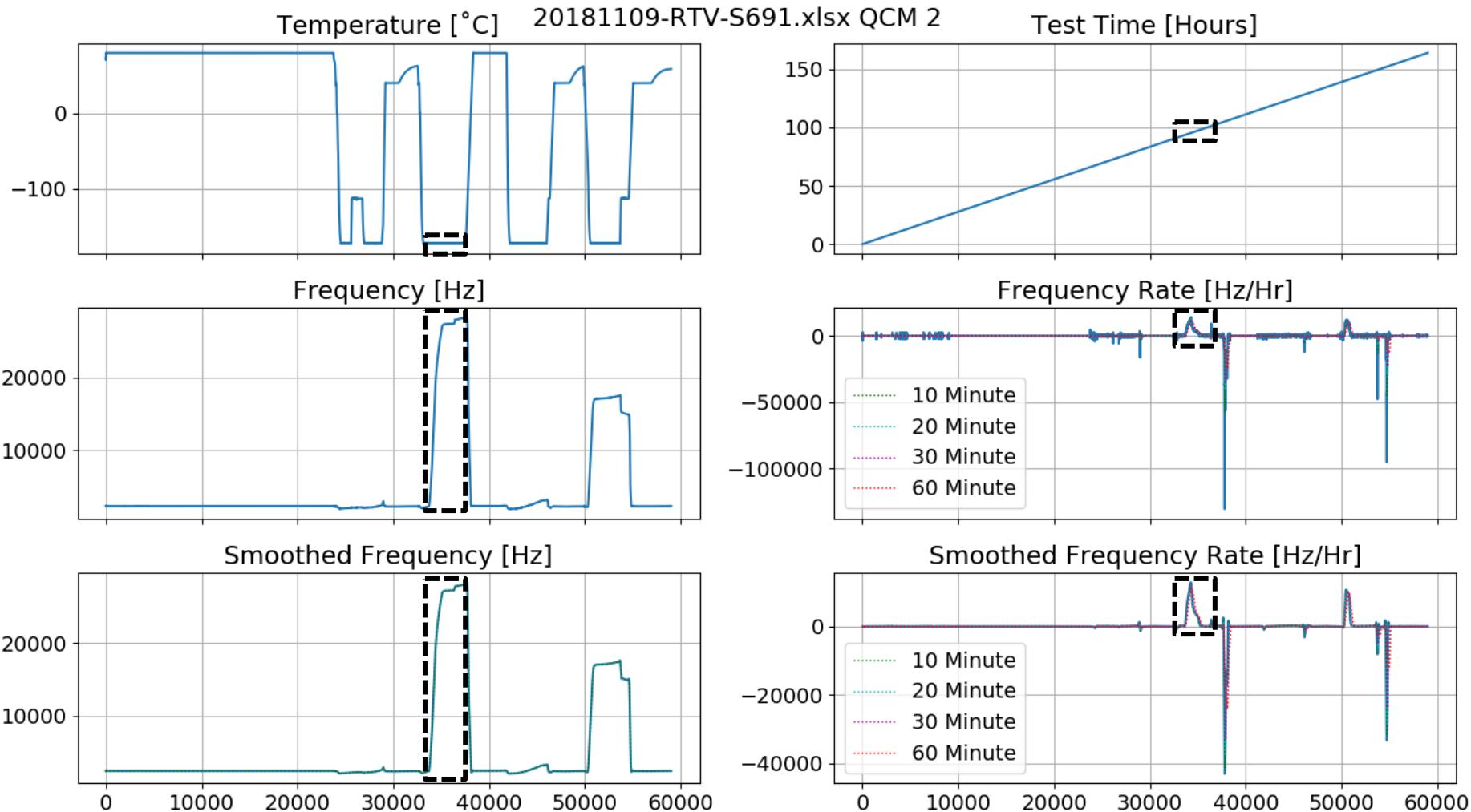
Nusil SCV-2596

- Silicone materials were mixed and applied per manufacturer specifications
- Cured for 7 days at room temperature
- Baked out at 110°C for 144 hours in $\leq 1E-05$ Torr

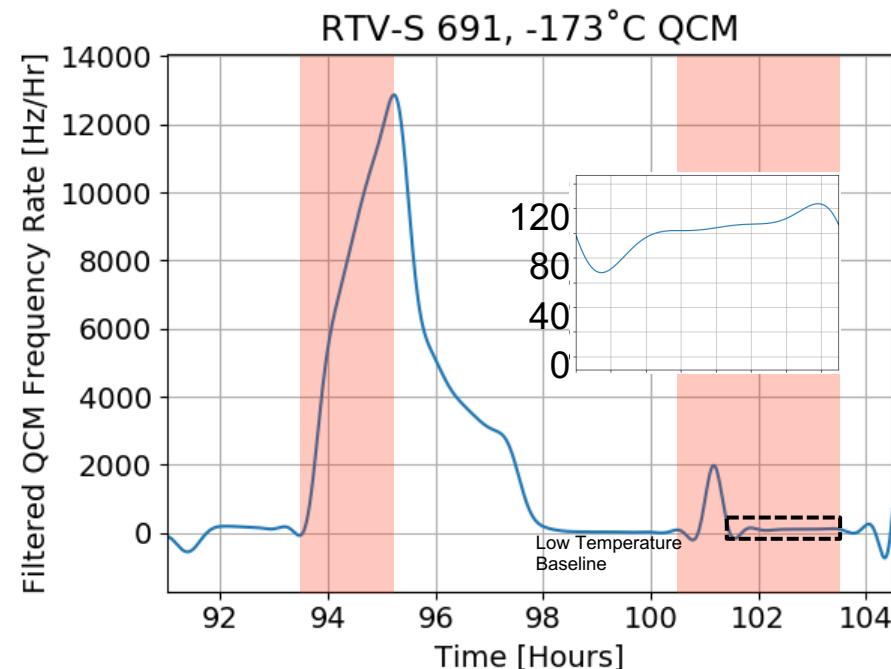
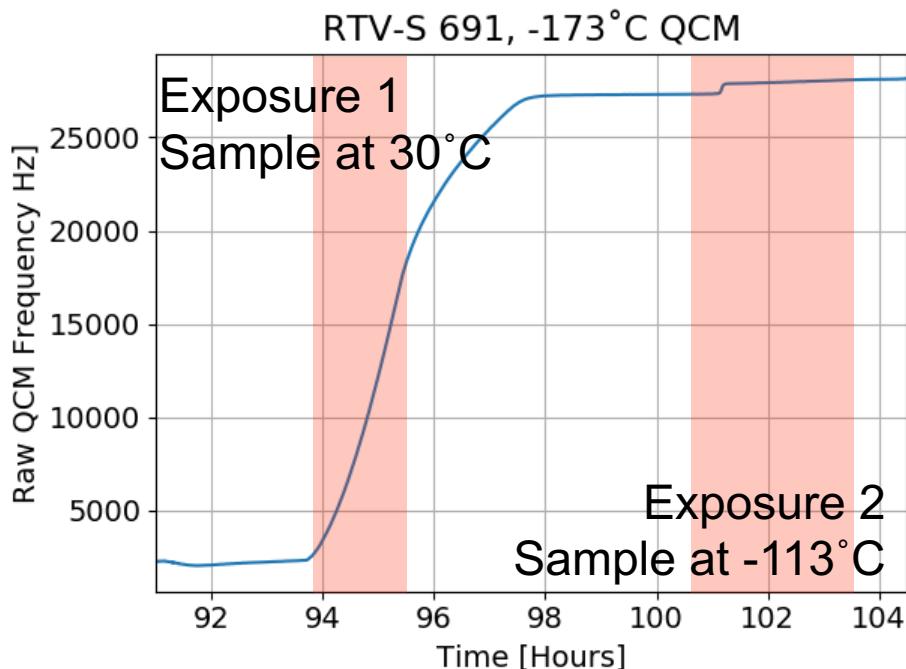
Pathfinder Test: RTV-S 691



Wacker RTV-S 691

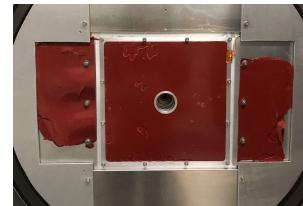


Expanded Test Section



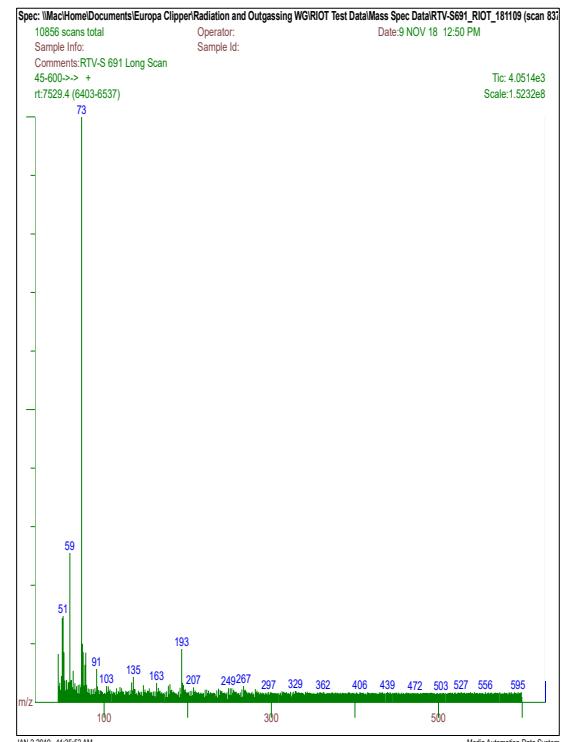
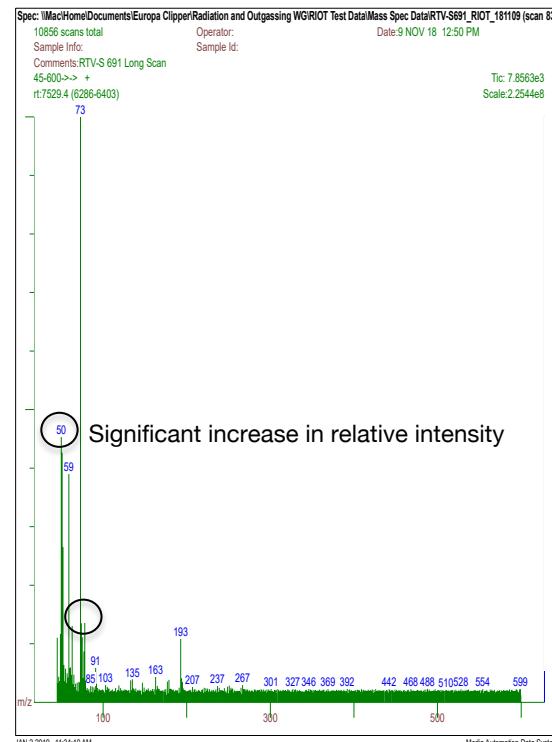
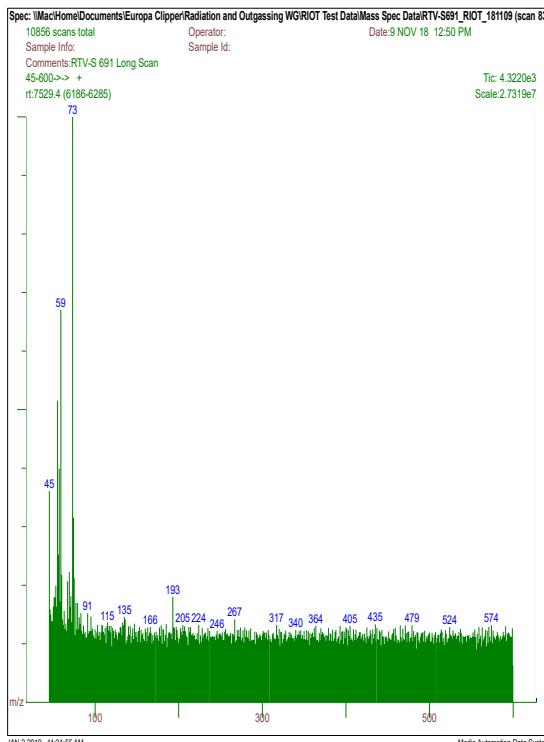
- Sample Temperature: +30°C
- Radiation exposure (1) at high temperature increases outgassing by orders of magnitude
- Termination of exposure 1 instantly begins decay of outgassing rate
- Low temperature radiation exposure (2) shows a more gradual but significant increase in outgassing rate above baseline levels

RTV-S 691 Mass Spectra Data Exposure 1

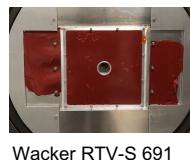


Wacker RTV-S 691

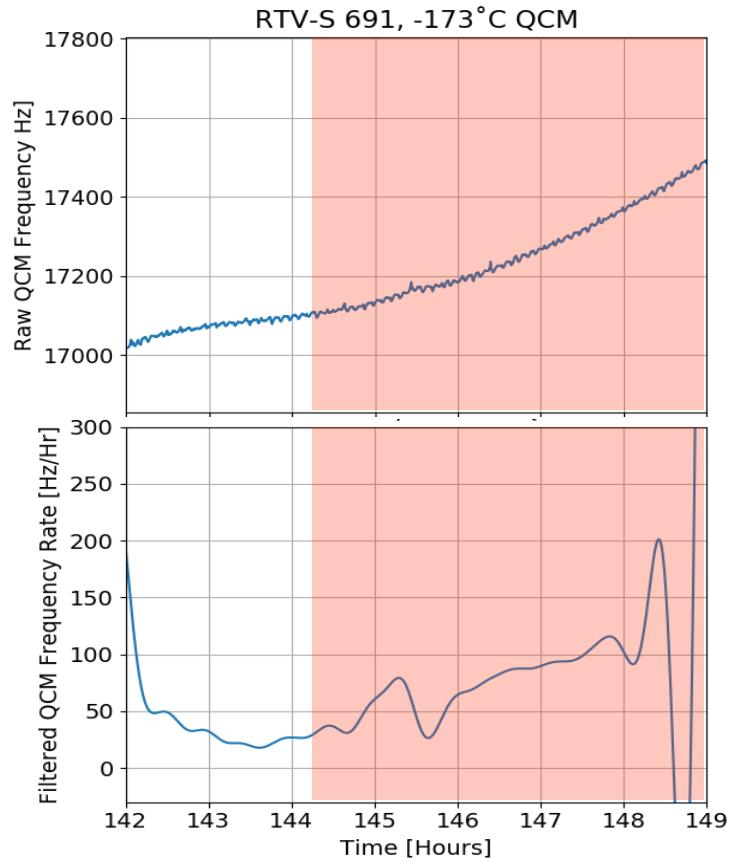
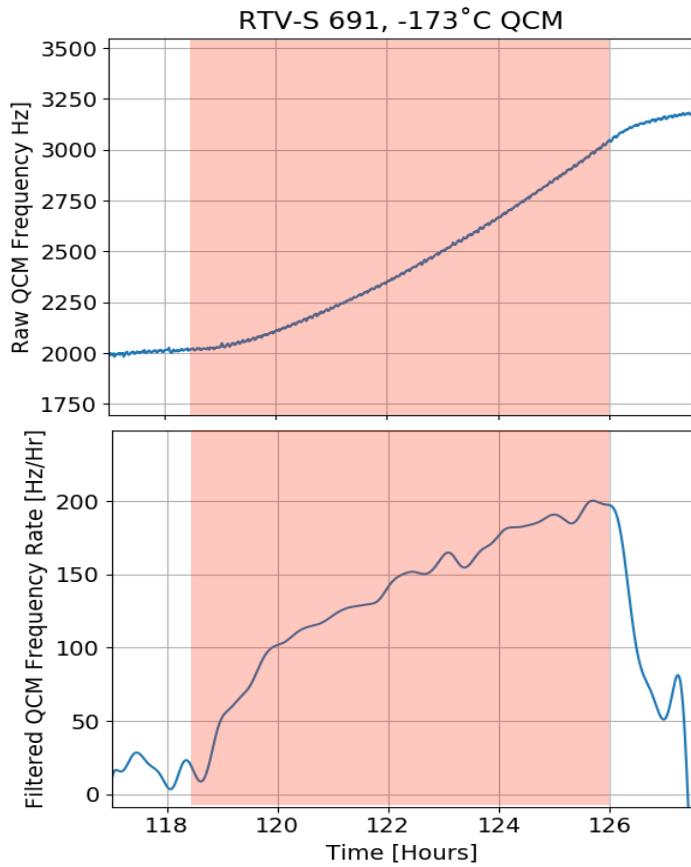
- Sample Temperature +30°C
- Relative intensities of species (50, 51, 52, 78 vs 73) change during irradiation
- Species during irradiation appear to be the same masses as without irradiation



RTV-S691 Repeatability Checks at Low Temperature (Exposures 3&4)

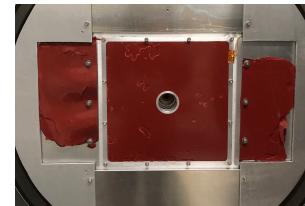


- Outgassing rates under irradiation approach approximately 200 Hz/Hr during both repeatability checks within an 8 hour exposure



Repeatability Check

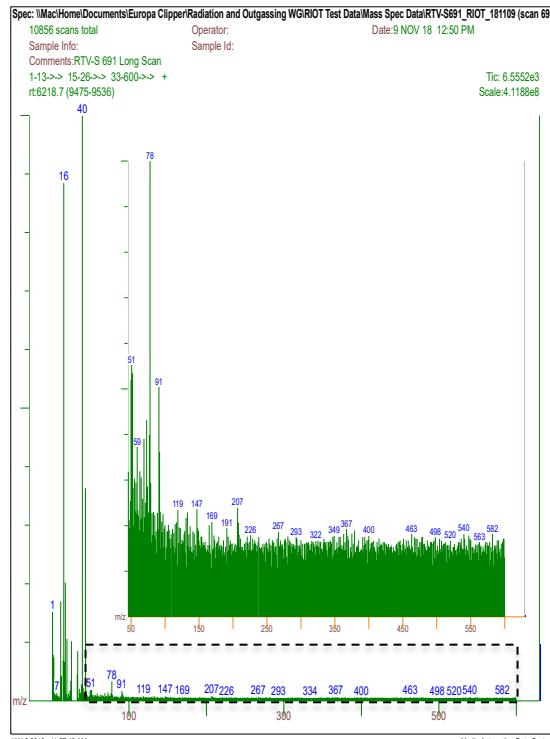
- Initial mass spectrum before irradiation has more pronounced silicone contaminant peaks
- Mass spectrum shows similar increases in contaminant peaks during and after irradiation
- Higher weight peaks appear after radiation than are seen before (281 specifically)



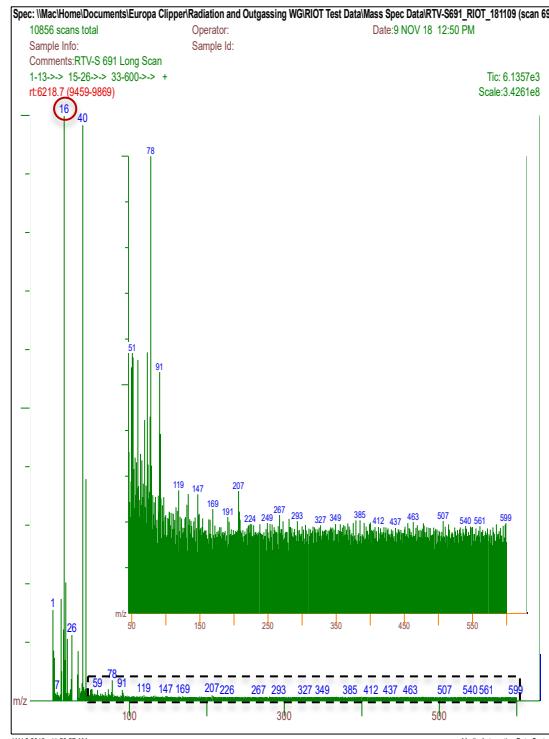
Wacker RTV-S 691

*scan range and MS tuning were change between these experiments

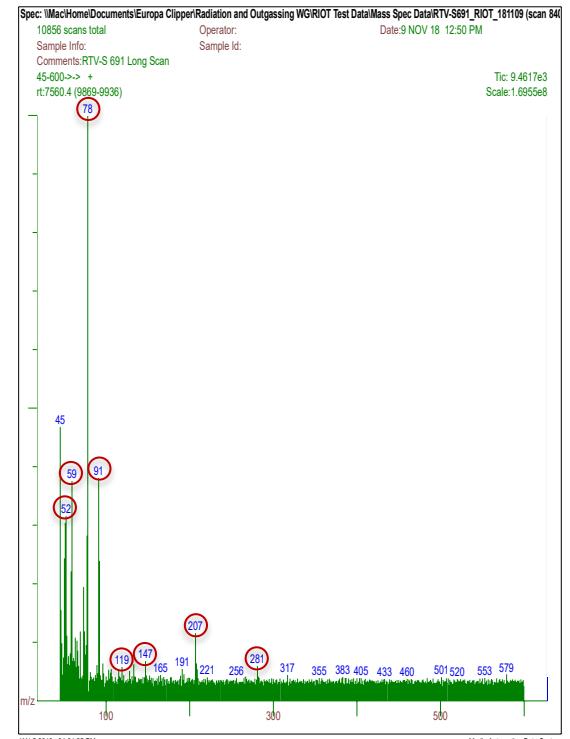
-113 °C Before Radiation



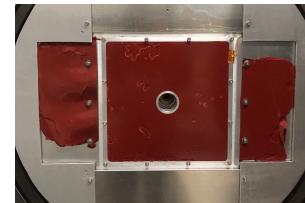
-113 °C During Radiation



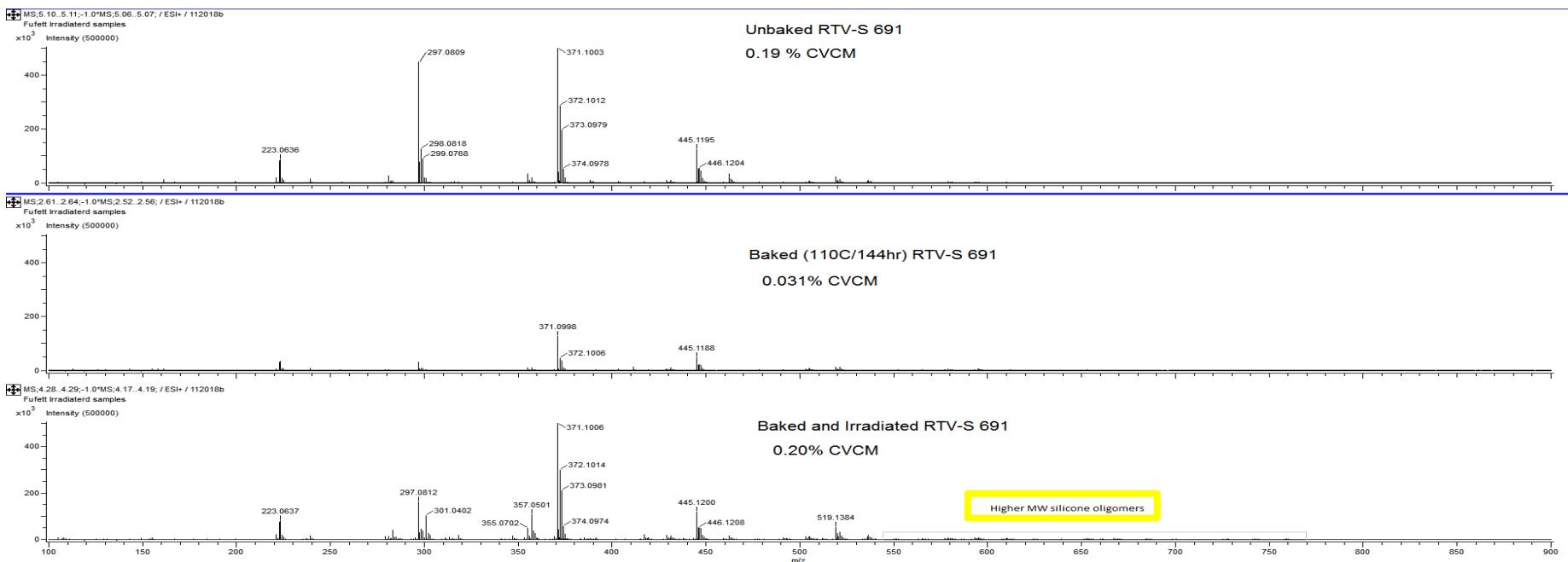
-113 °C After Radiation



Direct Analysis in Real Time (DART-MS) Results



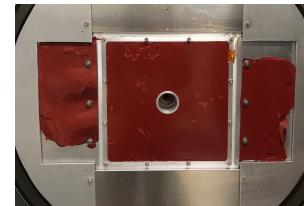
Wacker RTV-S 691



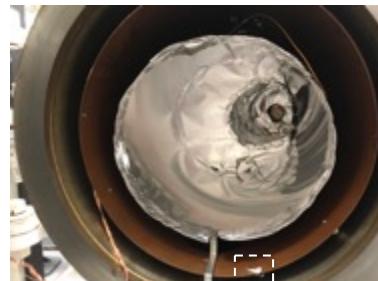
- DART-MS is a low energy mass spectrometry technique that yields primarily unfragmented parent species
- Analysis is of bulk material, may not be indicative of outgassed species
- Irradiated sample shows generation of high molecular weight (550 Da to 775 Da) silicone oligomers

Data and Results Provided By
JPL Analytical Chemistry Group

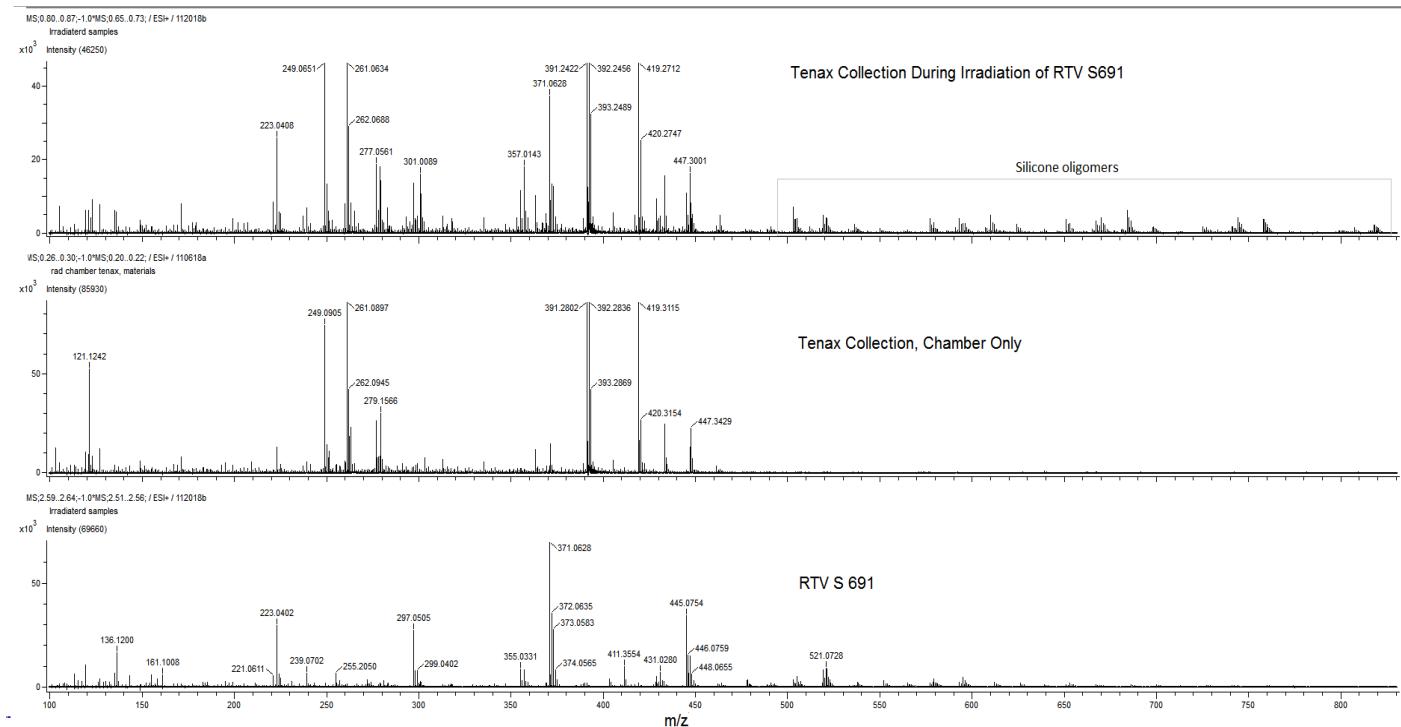
DART-MS of Tenax Getter in Dynamitron Vacuum Chamber



Wacker RTV-S 691

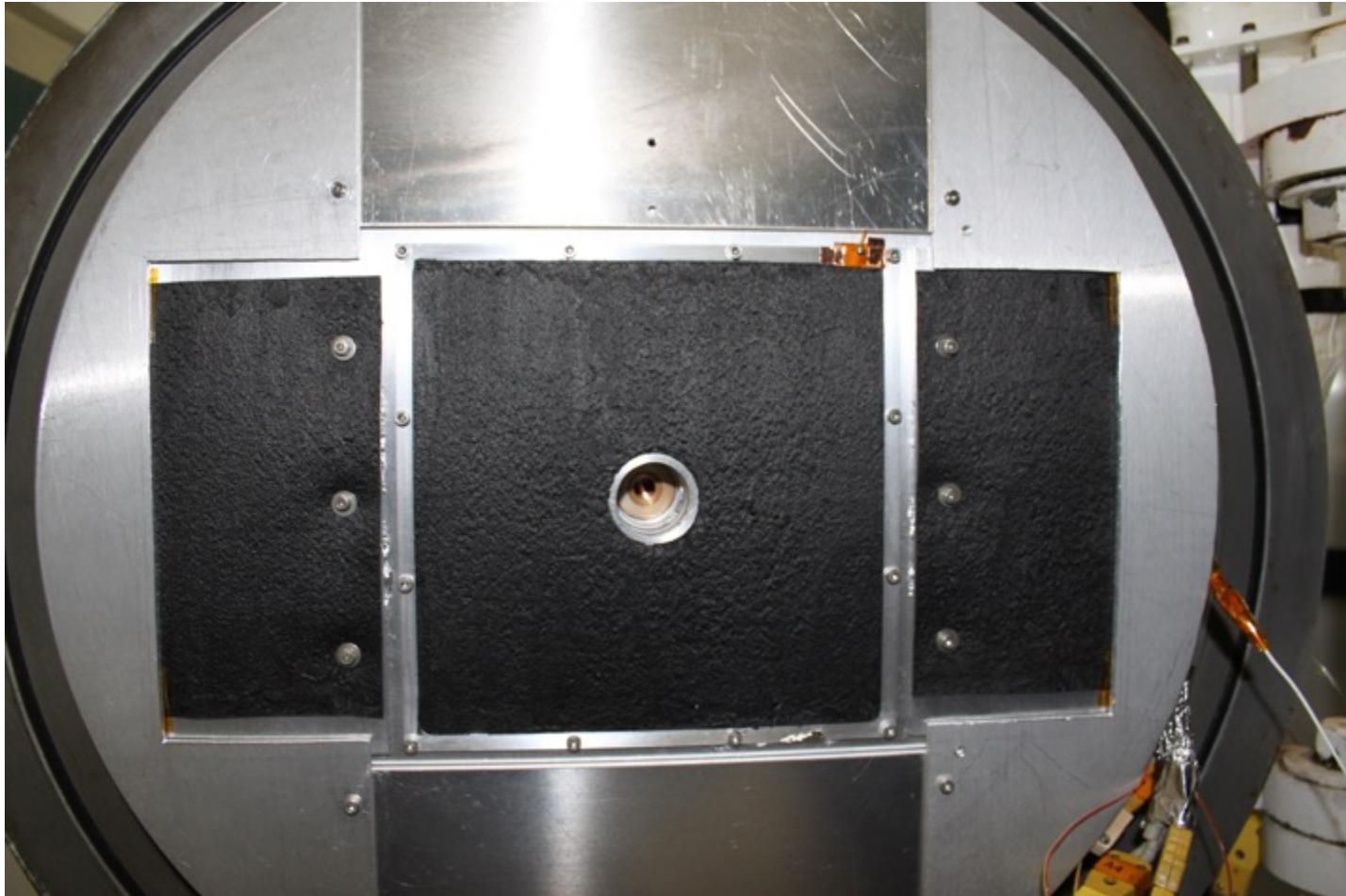


- Tenax molecular absorber was exposed in the Dynamitron vacuum chamber during RTV-S691 testing. A chamber run without RTV-S691 was previously run as a control.
- The Tenax collection during radiation (top) clearly shows the irradiated sample has a significant level of silicone oligomers being outgassed and collected in the Tenax. The chamber only run shows background volatiles (mid). For comparison, the RTV-S691 material analyzed directly by DART-MS



Data and Results Provided By
JPL Analytical Chemistry Group

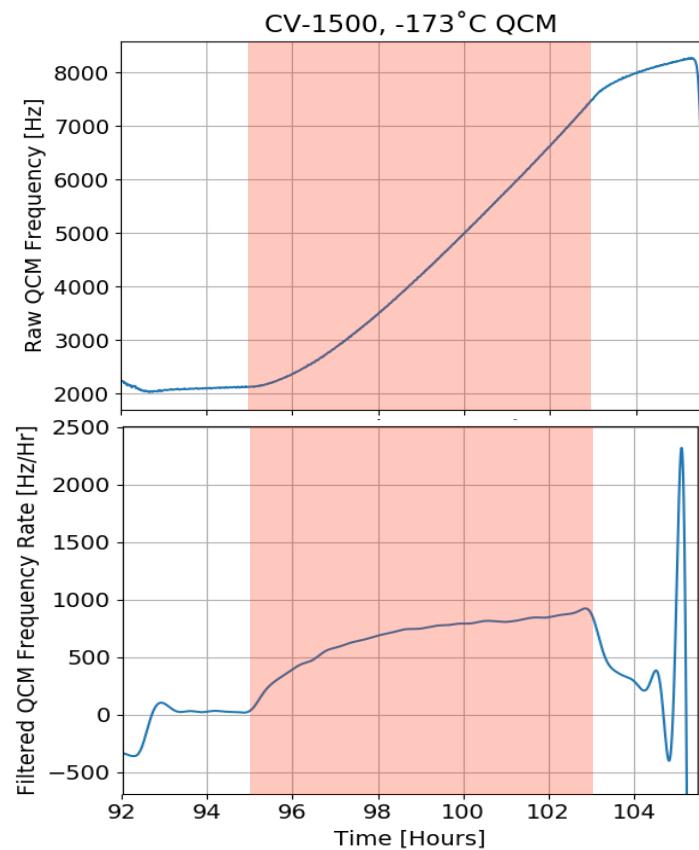
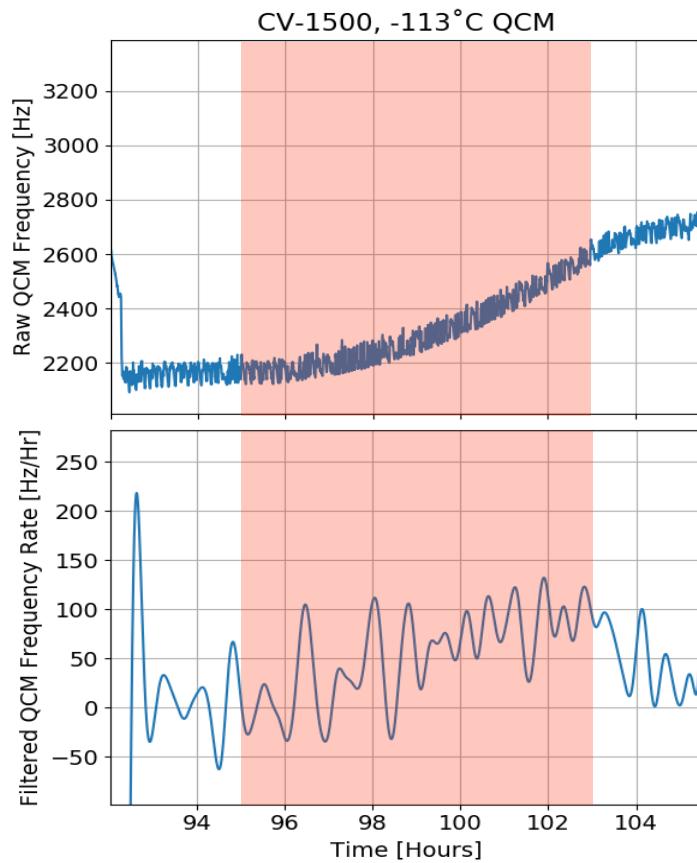
CV-1500 Conductive Silicone





CV-1500

- Radiation exposure impacted Nusil CV-1500 stronger than any other material tested
- The -173°C QCM increased to 950 Hz/Hr
- The -113°C QCM increased to 100 Hz/Hr



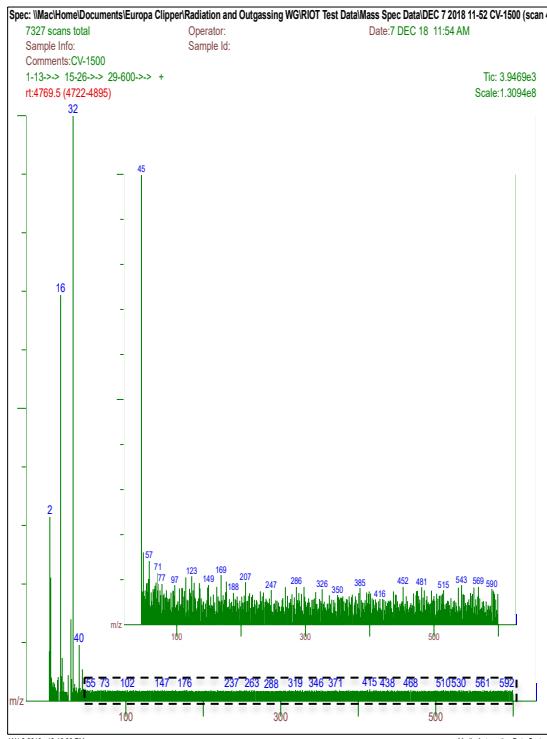


Mass Spectrometry for CV-1500

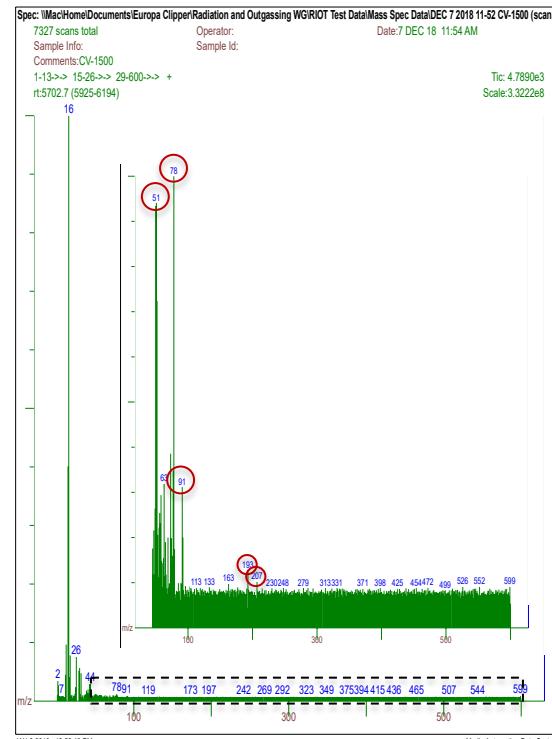
- CV-1500 shows evolution of MS peaks during and after radiation
 - silicones peaks ($m/z = 73, 91, 193, 207$)
 - Phenyl group peaks ($m/z = 50, 51, 52, 78$)

*scan range and MS tuning were change between these experiments

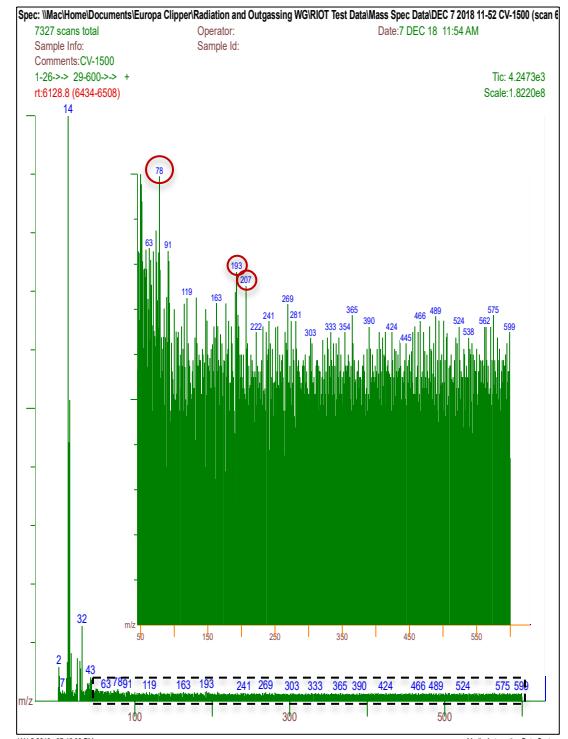
-113 °C Before Radiation



-113 °C During Radiation



-113 °C After Radiation



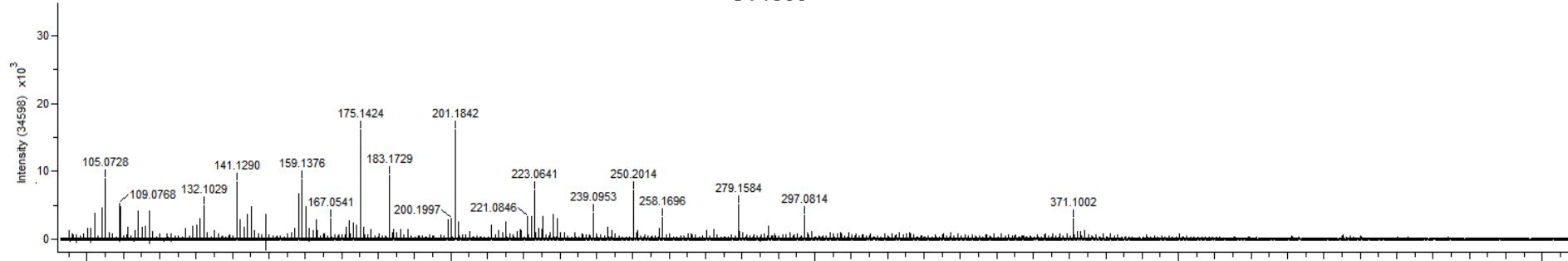


CV-1500 DART MS

Nusil CV-1500

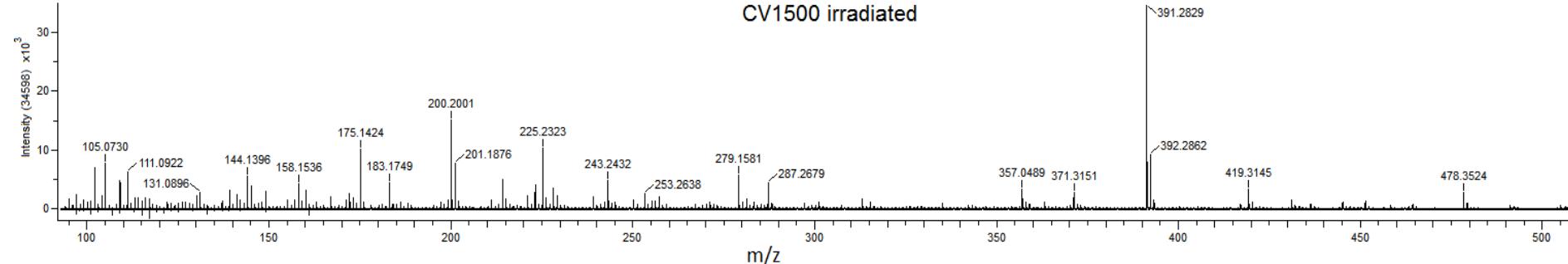
MS;5.00..5.05;-1.0*MS;4.62..4.72; / ESI+ / 121818b
A. Wong, RIOT

CV1500



MS;5.73..5.84;-1.0*MS;5.35..5.49; / ESI+ / 121818b
A. Wong, RIOT

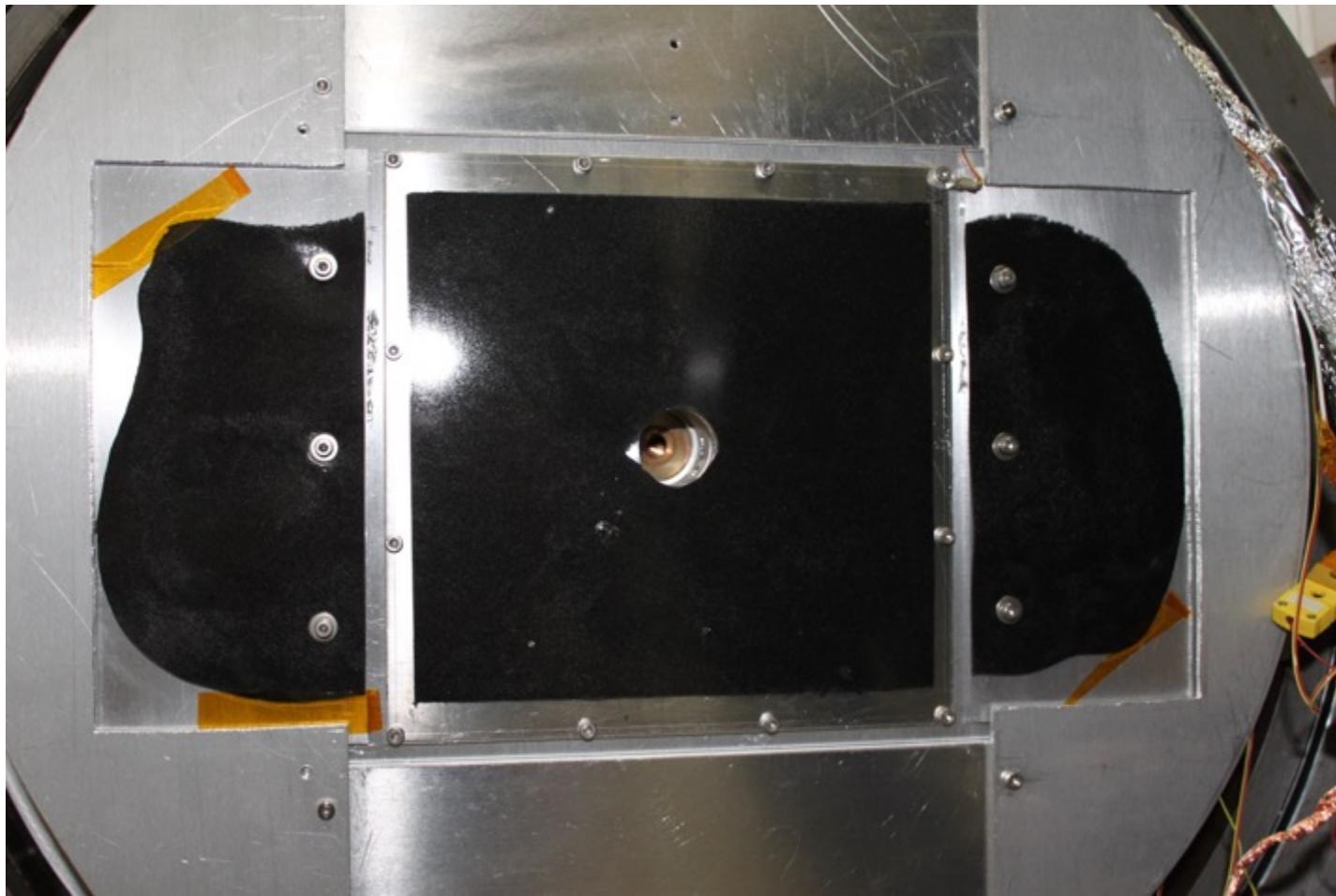
CV1500 irradiated

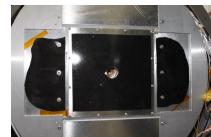


- Irradiated sample shows generation of high molecular weight (550 Da to 775 Da) silicone oligomers

Data and Results Provided By
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SCV-2596

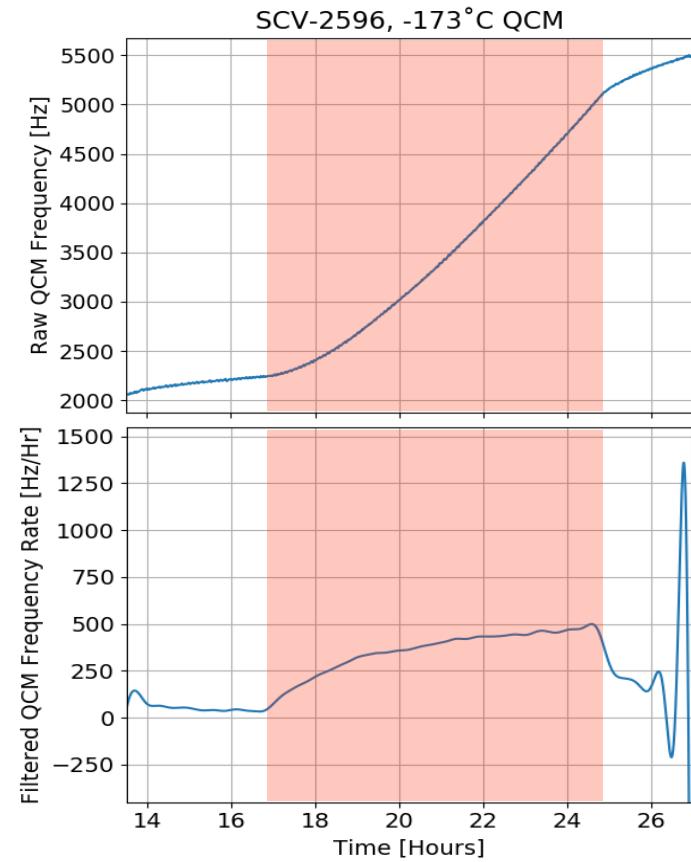
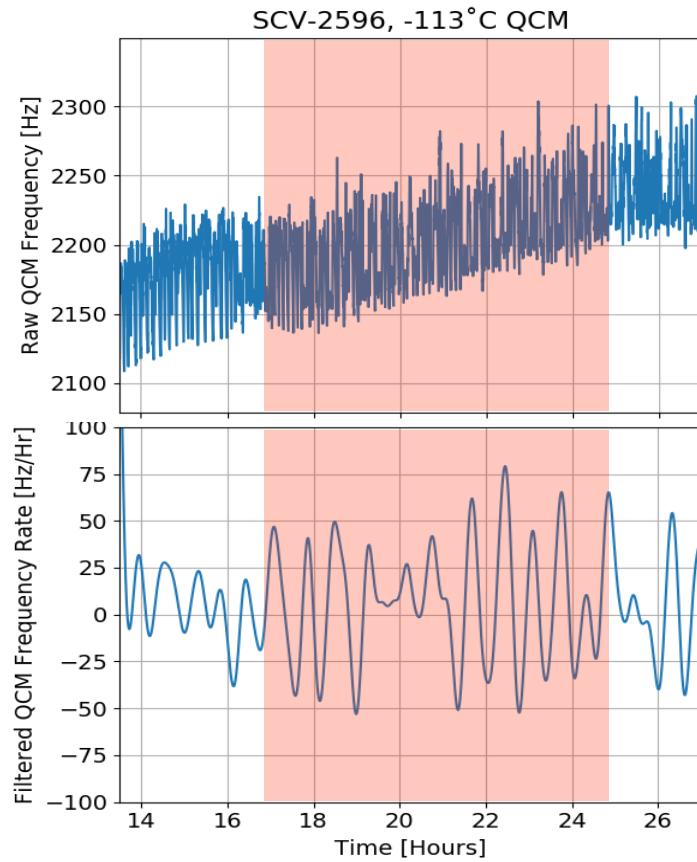


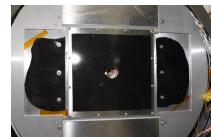


Nusil SCV-2596

SCV-2596 Conductive Silicone

- Super Controlled Volatility (SCV) is designed to be ultra low outgassing
- Radiation still increases outgassing rate by >10x
- The -173°C QCM increased to 500 Hz/Hr
- The -113°C QCM was not observed at any rate above background





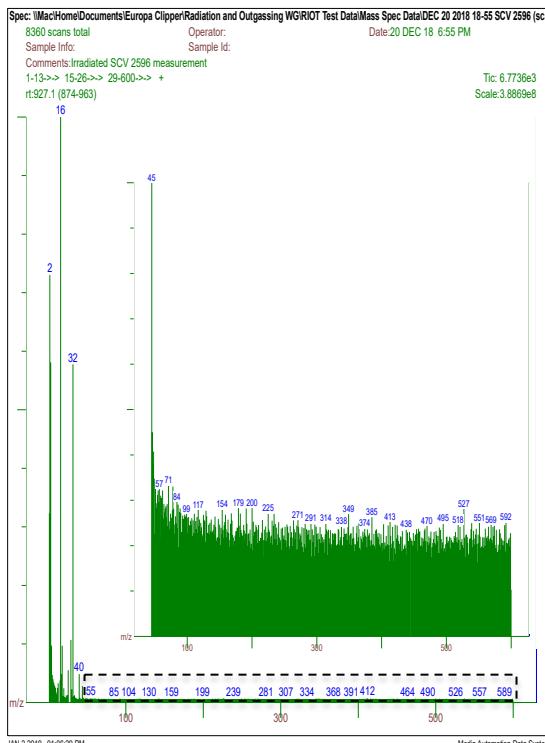
Nusil SCV-2596

Mass Spectrometry for SCV-2596

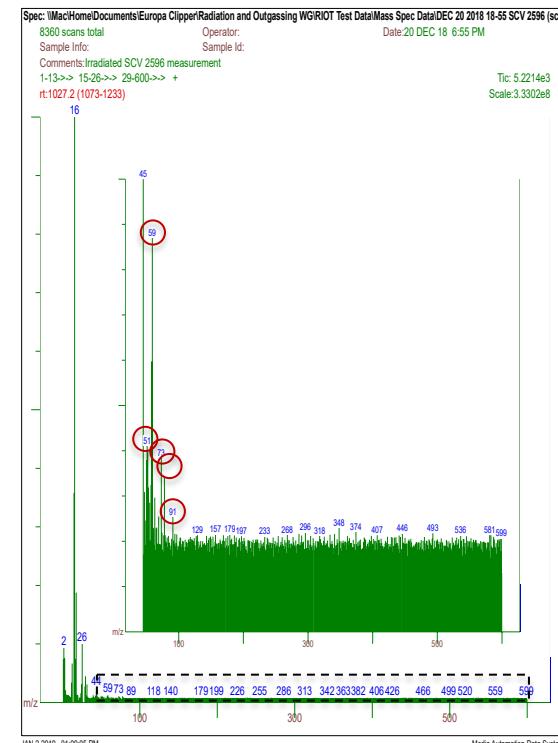
- SCV-2596 shows evolution of MS peaks
 - silicones peaks ($m/z = 73, 91$)
 - Phenyl group peaks ($m/z = 50, 51, 52, 78$)

*scan range and MS tuning were change between these experiments

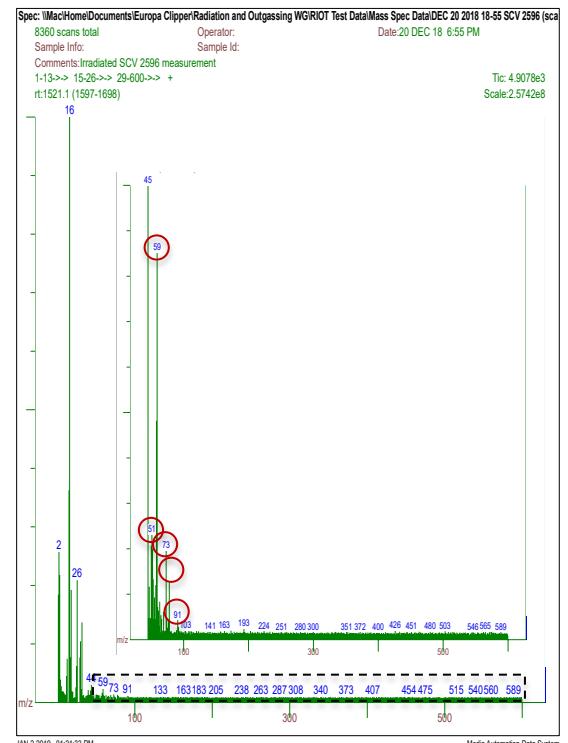
-113 °C Before Radiation



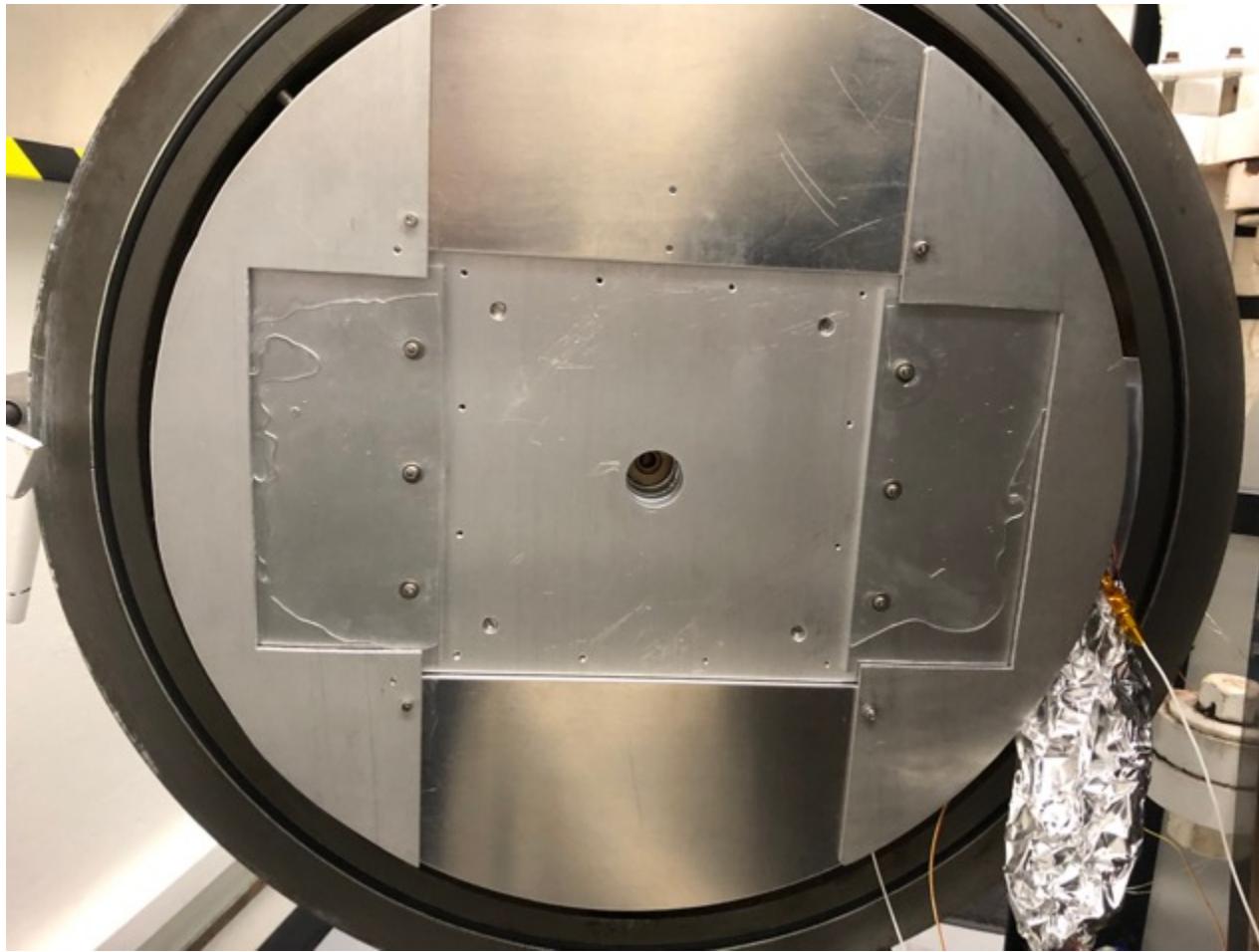
-113 °C During Radiation

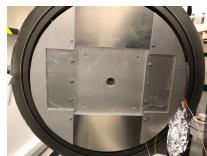


-113 °C After Radiation



SCV-2585

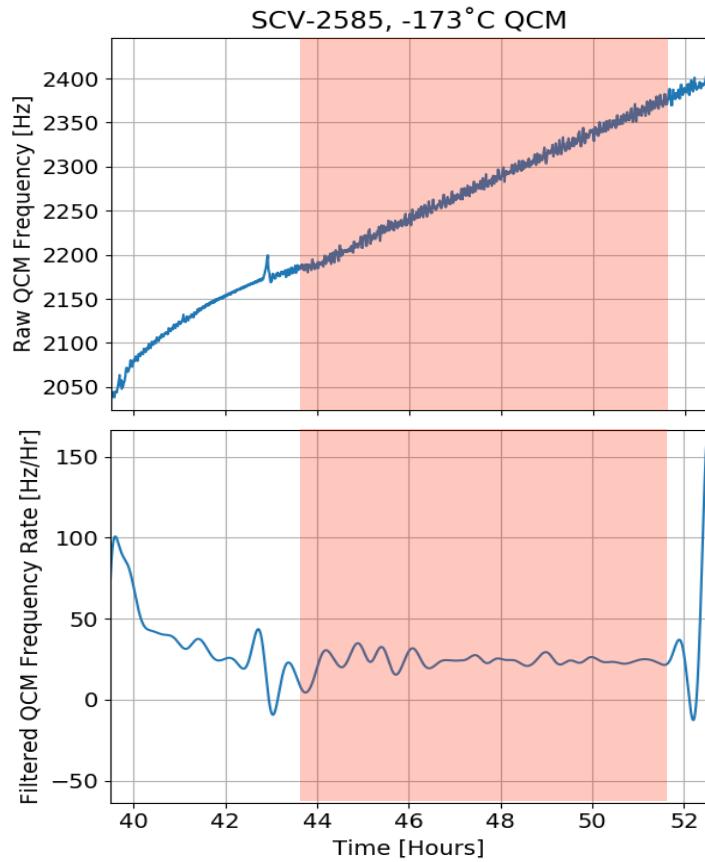
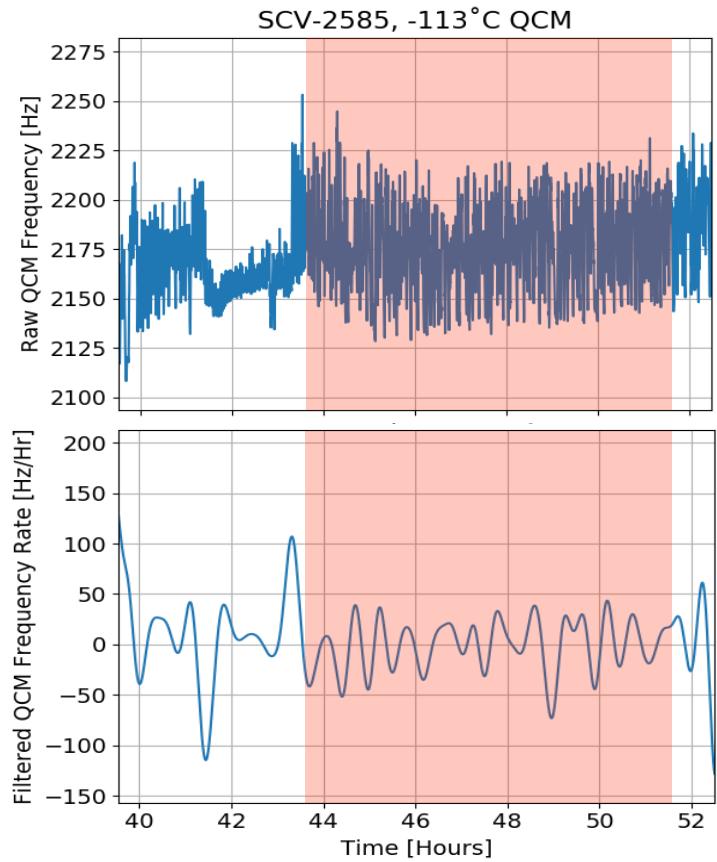




Nusil SCV-2585

SCV-2585

- Radiation exposure impacted Nusil CV-1500 stronger than any other material tested
- Neither QCM signal changed above the background



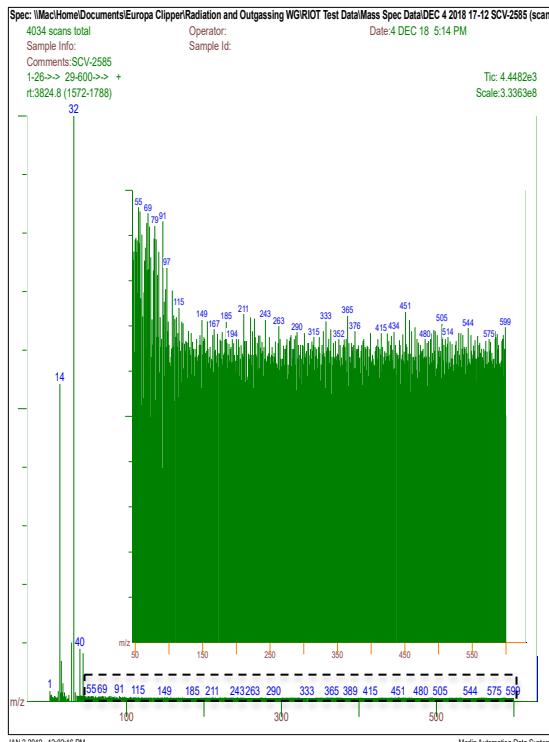


SCV-2585 Mass Spectrometry

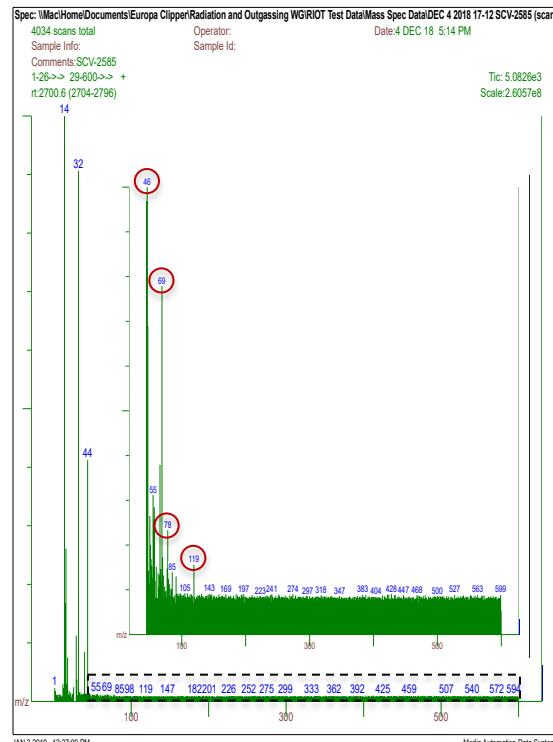
- SCV-2585 shows no significant changes in MS peaks
 - Minor increase in Masses 46,69,78, and 119

*scan range and MS tuning were change between these experiments

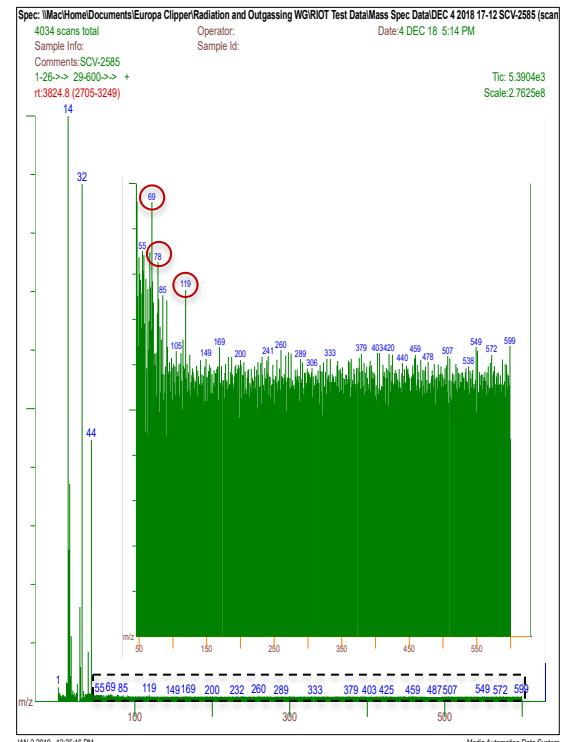
-113 °C Before Radiation

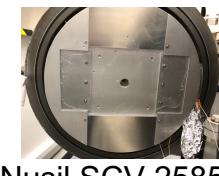


-113 °C During Radiation



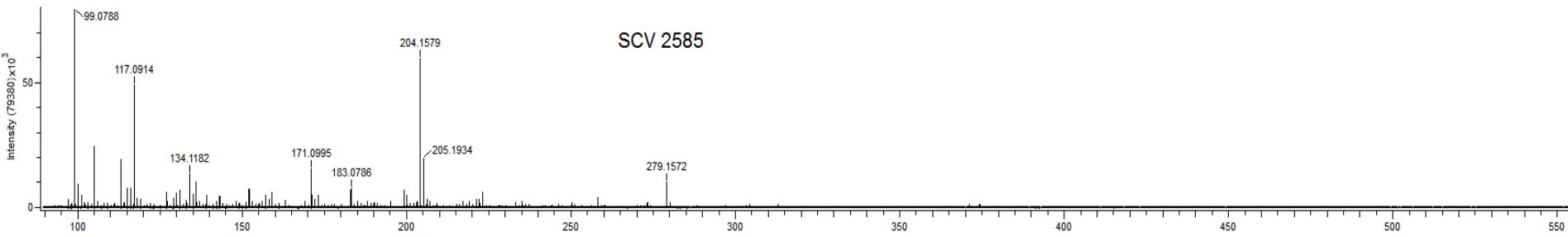
-113 °C After Radiation



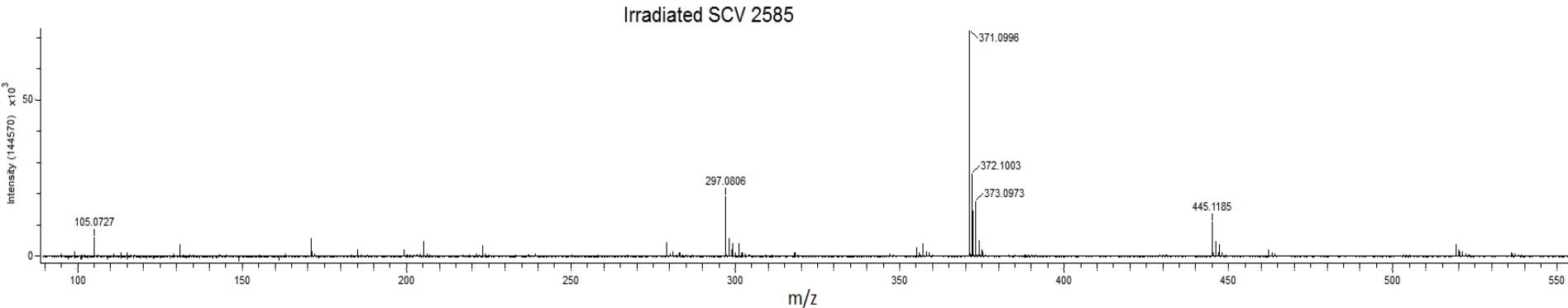


SCV-2585 DART-MS

MS,2.86..2.90;-1.0*MS,2.60..2.65; / ESI+ / 121818b
A. Wong, RIOT



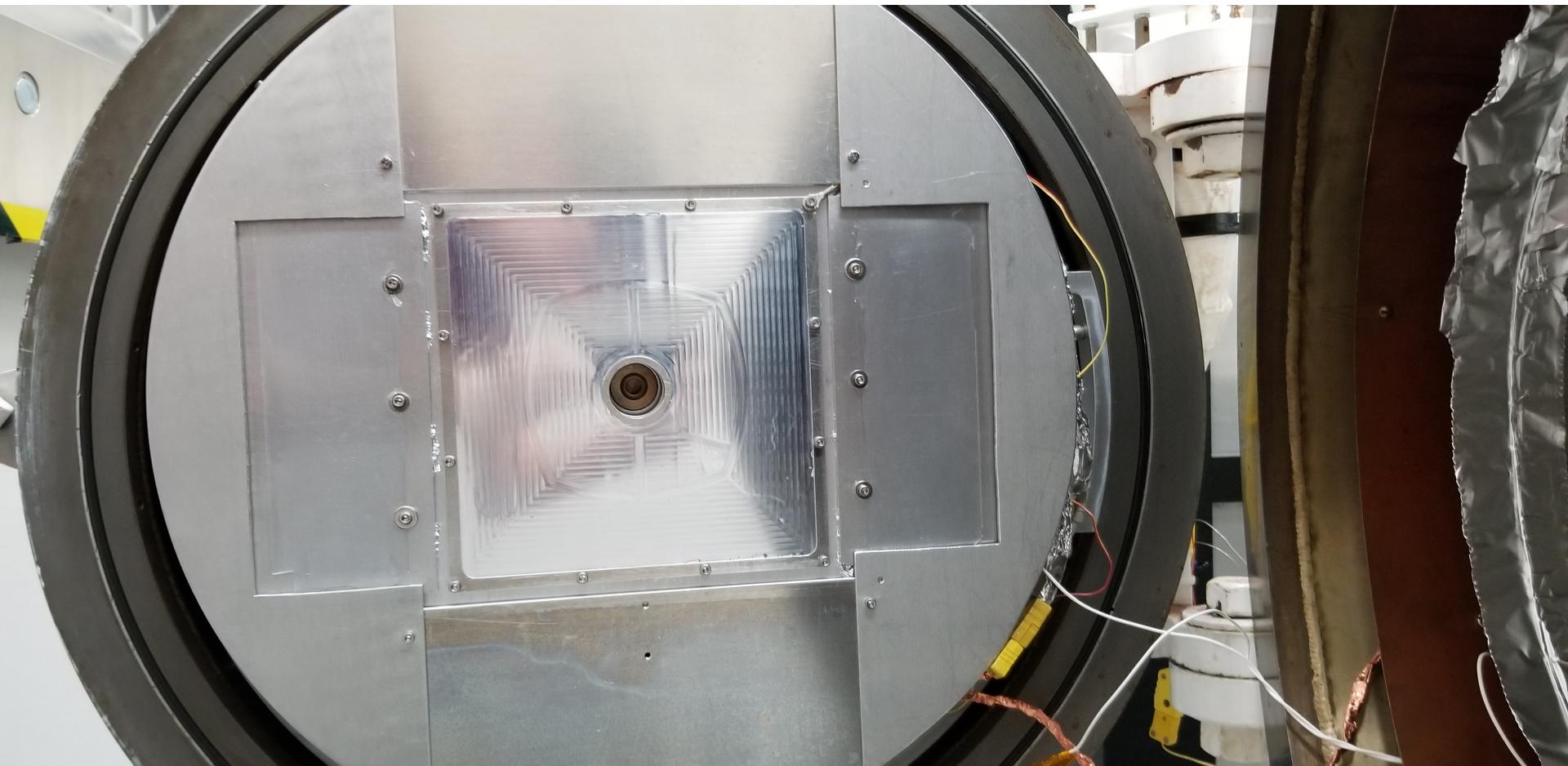
MS,3.67..3.70;-1.0*MS,3.54..3.62; / ESI+ / 121818b
A. Wong, RIOT



- Irradiated sample shows generation of high molecular weight (550 Da to 775 Da) silicone oligomers
- This increase is not reflected in the outgassing measurements

Data and Results Provided By
JPL Analytical Chemistry Group

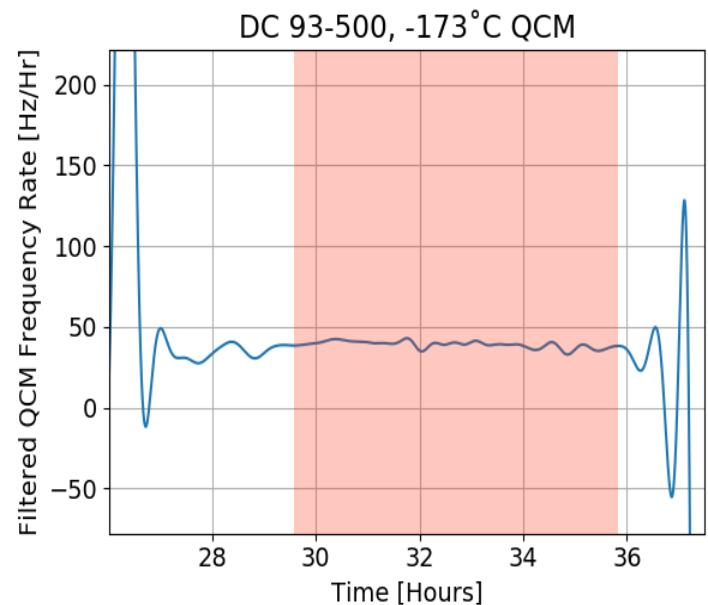
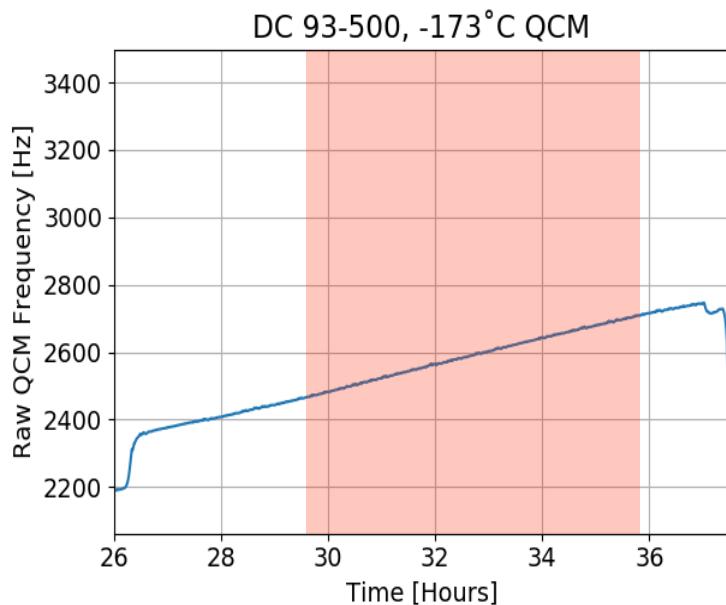
DC 93-500



DC 93-500



- 8 Hour Exposure demonstrates no change in outgassing rate
- Outgassing rate remains at background level for both QCMs

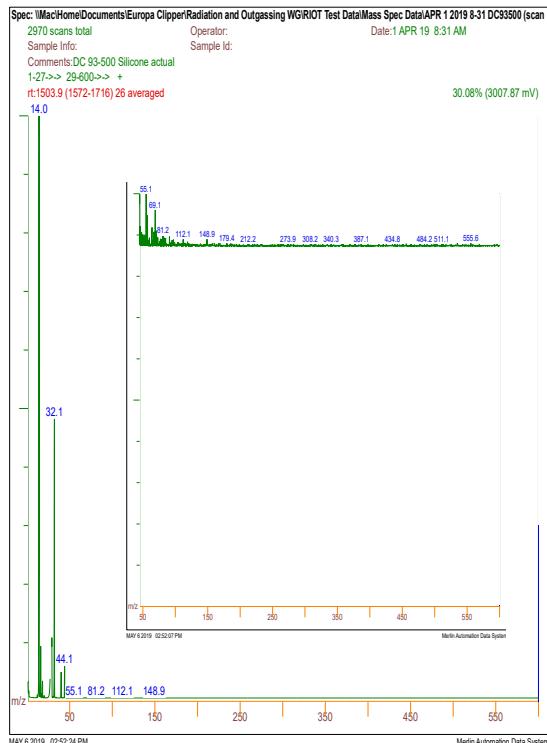




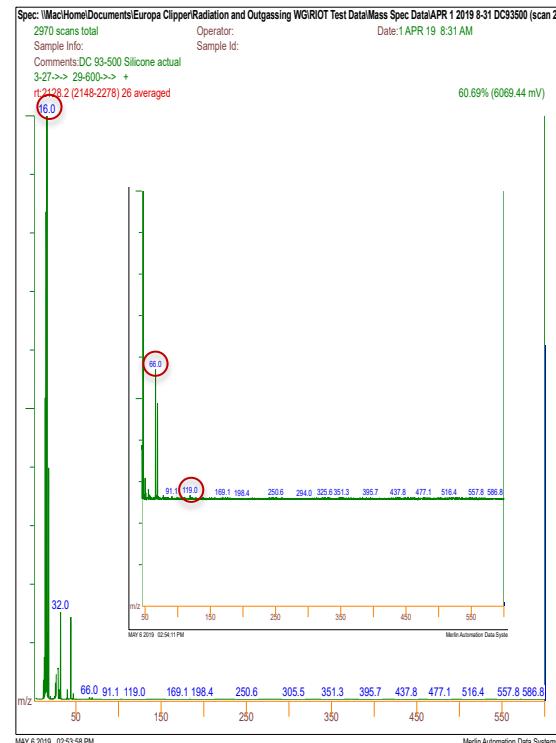
Mass Spectrometry for DC 93-500

- DC 93-500 shows no significant changes in MS peaks
 - Minor increase in Masses 66 and 119

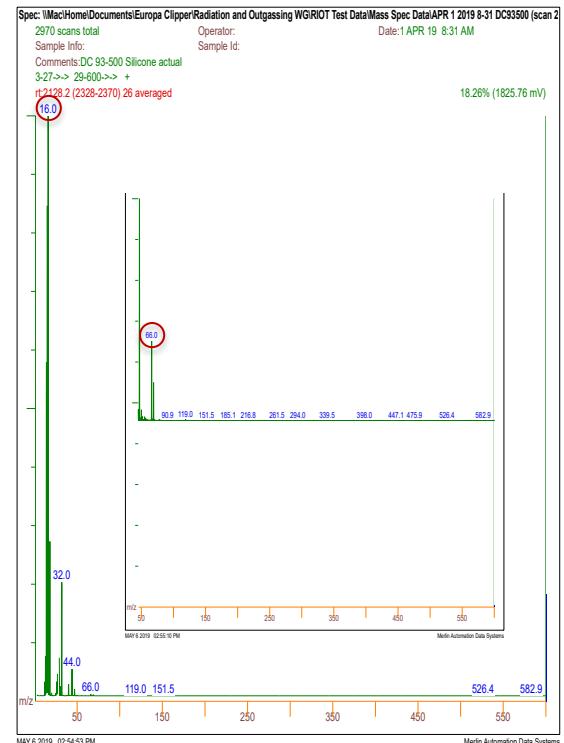
-113 °C Before Radiation



-113 °C During Radiation



-113 °C After Radiation

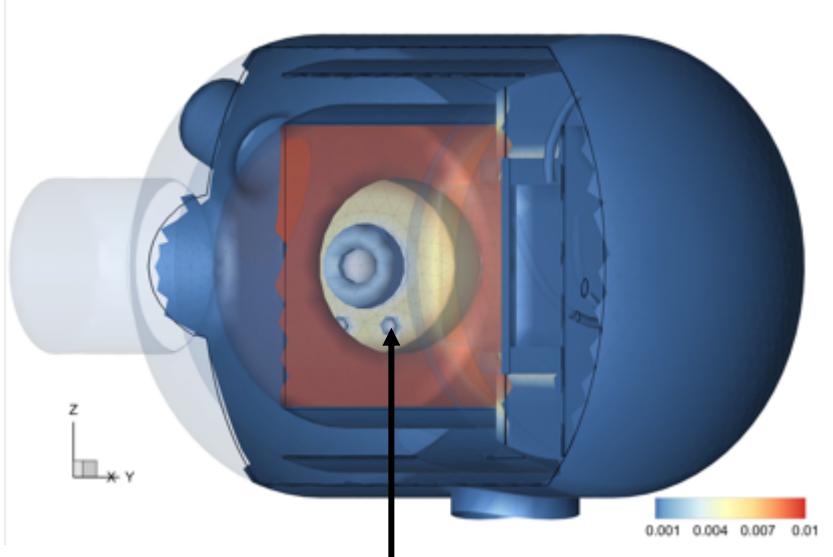


Transport Factor Bounding Cases

Analytic: 0.045%

Calculated by creating geometric model of chamber and modeling molecular flow from sample

ASEC Presentation on Friday at 8:50 am by Dr. William Hoey



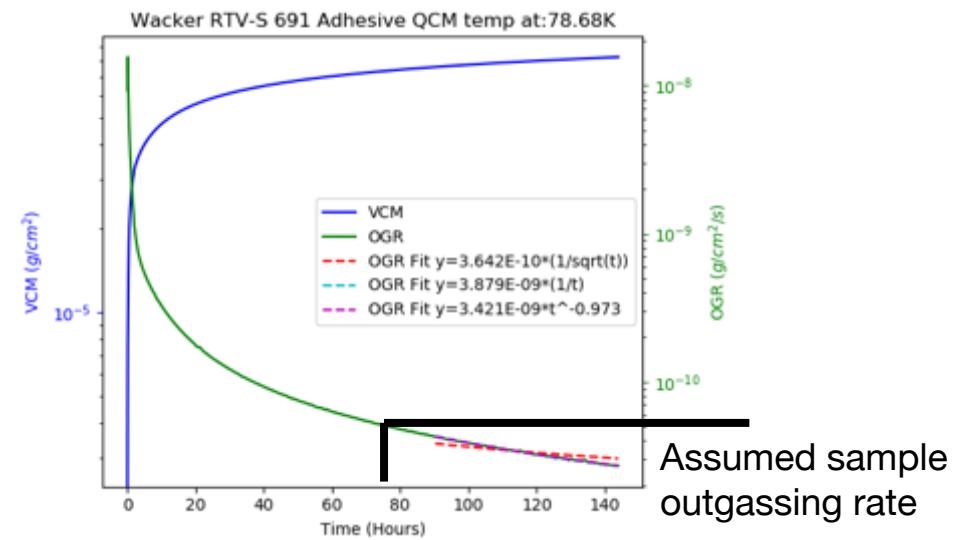
Transport factor calculated to QCM surfaces

Experimental: 0.28%

Calculated by comparing ASTM-E1559 data to chamber measurements

Assumptions:

- Sample has outgassing rate as measured by ASTM-E1559
- Chamber 100K QCM collects the same material as ASTM-E1559's 80K QCM



Assumed sample outgassing rate

Combined Results of RIOT Testing

-173°C QCM Results

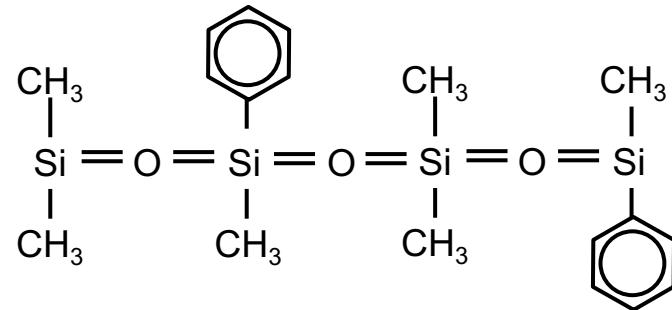
Silicone Sample	Sample Color	Primary Property	Final Irradiated Outgassing Rate [Hz/Hr]
Wacker RTV-S 691	Red	Yield Strength	~200
Nusil CV-1500	Black	Conductive	~950
Nusil SCV-2596	Black	Conductive	~500
Nusil SCV-2585	Clear	Yield Strength	~25 (Background)
DC 93-500	Clear	Optical Transparency	~40 (Background)

Mass Spectra Results

Silicone Sample	Mass Signal Increases Due to Irraditaion	Identified Species
Wacker RTV-S 691	16, 50, 51, 52, 78, 59, 91, 147, 207, 281	Oxygen, Silicones, Phenyl Group
Nusil CV-1500	16, 50, 51, 52, 78, 92, 193, 207	Oxygen, Silicones, Phenyl Group
Nusil SCV-2596	16, 51, 59, 73, 78, 91	Oxygen, Silicones, Phenyl Group
Nusil SCV-2585	16, 46, 69, 78, 119	Oxygen,
DC 93-500	16, 66, 119	Oxygen, Silicones

Conclusions

- Pure Silicone materials (SCV-2585 and DC 93-500) demonstrated no increase in outgassing from radiation exposure
- Materials with filler (RTV-S691, CV-1500, SCV-2596) all showed continuous increases with respect to time during radiation exposure
- Outgassing rates fall off when radiation exposure is terminated
- Mass Spectra of irradiated samples yield the same mass constituents (no new species) but at different relative intensities





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Backup: Proposed Mechanism

- Bond scission can occur at any bond in the silicone structure
- Functional groups break off and diffuse quickly out of the bulk
- Silicone backbone breaks but diffuses more slowly
- Breaks in the silicone backbone create radical sites that can recombine

